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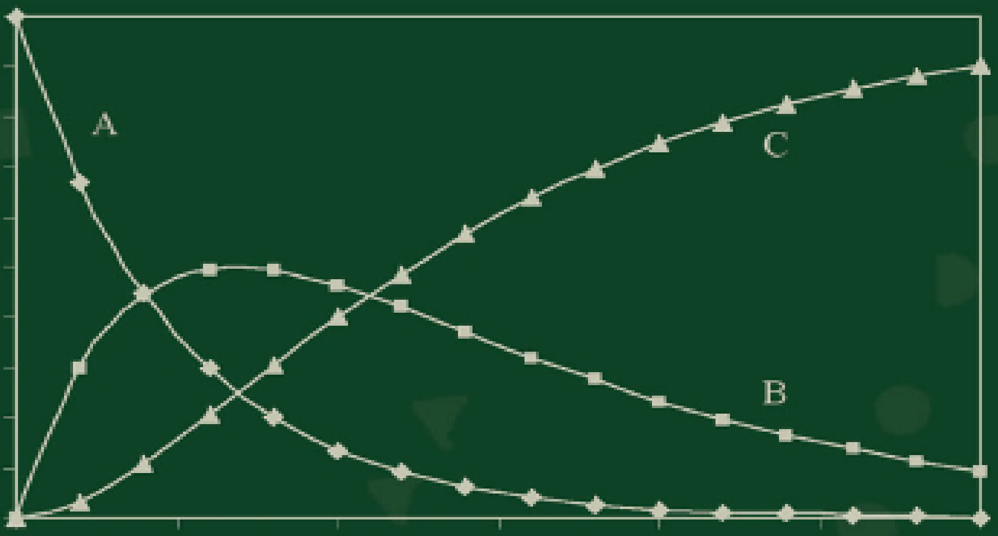
CHEMICAL KINETICS



SECOND EDITION

JAMES E. HOUSE

Principles of Chemical Kinetics

Principles of Chemical Kinetics

Second Edition

James E. House
Illinois State University
and
Illinois Wesleyan University

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Preface

Chemical kinetics is an enormous field that has been the subject of many books, including a series that consists of numerous large volumes. To try to cover even a small part of the field in a single volume of portable size is a difficult task. As is the case with every writer, I have been forced to make decisions on what to include, and like other books, this volume reflects the interests and teaching experience of the author.

As with the first edition, the objective has been to provide an introduction to most of the major areas of chemical kinetics. The extent to which this has been done successfully will depend on the viewpoint of the reader. Those who study only gas phase reactions will argue that not enough material has been presented on that topic. A biochemist who specializes in enzyme-catalyzed reactions may find that research in that area requires additional material on the topic. A chemist who specializes in assessing the influence of substituent groups or solvent on rates and mechanisms of organic reactions may need other tools in addition to those presented. In fact, it is fair to say that this book is not written for a *specialist* in any area of chemical kinetics. Rather, it is intended to provide readers an introduction to the major areas of kinetics and to provide a basis for further study. In keeping with the intended audience and purposes, derivations are shown in considerable detail to make the results readily available to students with limited background in mathematics.

In addition to the significant editing of the entire manuscript, new sections have been included in several chapters. Also, Chapter 9 ''Additional Applications of Kinetics,'' has been added to deal with some topics that do not fit conveniently in other chapters. Consequently, this edition contains substantially more material, including problems and references, than the first edition. Unlike the first edition, a solution manual is also available.

As in the case of the first edition, the present volume allows for variations in the order of taking up the material. After the first three chapters, the

remaining chapters can be studied in any order. In numerous places in the text, attention is drawn to the fact that similar kinetic equations result for different types of processes. As a result, it is hoped that the reader will see that the assumptions made regarding interaction of an enzyme with a substrate are not that different from those regarding the adsorption of a gas on the surface of a solid when rate laws are derived. The topics dealing with solid state processes and nonisothermal kinetics are covered in more detail than in some other texts in keeping with the growing importance of these topics in many areas of chemistry. These areas are especially important in industrial laboratories working on processes involving the drying, crystallizing, or characterizing of solid products.

It is hoped that the present volume will provide a succinct and clear introduction to chemical kinetics that meets the needs of students at a variety of levels in several disciplines. It is also hoped that the principles set forth will prove useful to researchers in many areas of chemistry and provide insight into how to interpret and correlate their kinetic data.

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CHAPTER 1

Fundamental Concepts of Kinetics

It is frequently observed that reactions that lead to a lower overall energy state as products are formed take place readily. However, there are also many reactions that lead to a decrease in energy, yet the rates of the reactions are low. For example, the heat of formation of water from gaseous H_2 and O_2 is −285 kJ/mol, but the reaction

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \tag{1.1}$$

takes place very slowly, if at all, unless the reaction is initiated by a spark. The reason for this is that although a great deal of energy is released as H_2O forms, there is no low energy pathway for the reaction to follow. In order for water to form, molecules of H_2 and O_2 must react, and their bond energies are about 435 and 490 kJ/mol, respectively.

Thermodynamics is concerned with the overall energy change between the initial and final states for a process. If necessary, this change can result after an infinite time. Accordingly, thermodynamics does not deal with the subject of reaction *rates*, at least not directly. The preceding example shows that the *thermodynamics* of the reaction favors the production of water; however, *kinetically* the process is unfavorable. We see here the first of several important principles of chemical kinetics. There is no necessary correlation between thermodynamics and kinetics of a chemical reaction. Some reactions that are energetically favorable take place very slowly because there is no low energy pathway by which the reaction can occur.

One of the observations regarding the study of reaction rates is that a rate cannot be calculated from first principles. Theory is not developed to the point where it is possible to calculate how fast most reactions will take place. For some very simple gas phase reactions, it is possible to calculate approximately how fast the reaction should take place, but details

of the process must usually be determined experimentally. Chemical kinetics is largely an experimental science.

Chemical kinetics is intimately connected with the analysis of data. The personal computers of today bear little resemblance to those of a couple of decades ago. When one purchases a computer, it almost always comes with software that allows the user to do much more than word processing. Software packages such as Excel, Mathematica, MathCad, and many other types are readily available. The tedious work of plotting points on graph paper has been replaced by entering data in a spreadsheet. This is not a book about computers. A computer is a *tool*, but the user needs to know how to interpret the results and how to choose what types of analyses to perform. It does little good to find that some mathematics program gives the best fit to a set of data from the study of a reaction rate with an arctangent or hyperbolic cosine function. The point is that although it is likely that the reader may have access to data analysis techniques to process kinetic data, the purpose of this book is to provide the background in the principles of kinetics that will enable him or her to interpret the results. The capability of the available software to perform numerical analysis is a separate issue that is not addressed in this book.

1.1 RATES OF REACTIONS

The rate of a chemical reaction is expressed as a change in concentration of some species with time. Therefore, the dimensions of the *rate* must be those of concentration divided by time (moles/liter sec, moles/liter min, etc.). A reaction that can be written as

$$\mathrm{A} \rightarrow \mathrm{B} \tag{1.2}$$

has a rate that can be expressed either in terms of the disappearance of A or the appearance of B. Because the concentration of A is *decreasing* as A is consumed, the rate is expressed as $-d[\mathrm{A}]/dt$. Because the concentration of B is *increasing* with time, the rate is expressed as $+d[\mathrm{B}]/dt$. The mathematical equation relating concentrations and time is called the *rate equation* or the *rate law*. The relationships between the concentrations of A and B with time are represented graphically in Figure 1.1 for a first-order reaction in which $[\mathrm{A}]_o$ is 1.00 **M** and $k = 0.050\,\mathrm{min}^{-1}$.

If we consider a reaction that can be shown as

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D} \tag{1.3}$$

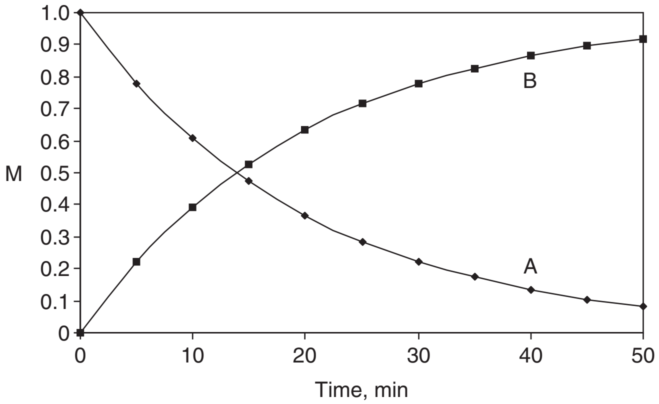


FIGURE 1.1 Change in concentration of A and B for the reaction A → B.

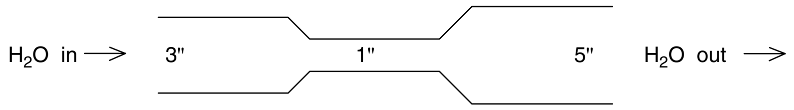
the rate law will usually be represented in terms of a constant times some function of the concentrations of A and B, and it can usually be written in the form

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y \tag{1.4}$$

where x and y are the exponents on the concentrations of A and B, respectively. In this rate law, k is called the rate constant and the exponents x and y are called the *order* of the reaction with respect to A and B, respectively. As will be described later, the exponents x and y may or may not be the same as the balancing coefficients a and b in Eq. (1.3). The overall order of the reaction is the sum of the exponents x and y. Thus, we speak of a second-order reaction, a third-order reaction, etc., when the sum of the exponents in the rate law is 2, 3, etc., respectively. These exponents can usually be established by studying the reaction using different initial concentrations of A and B. When this is done, it is possible to determine if doubling the concentration of A doubles the rate of the reaction. If it does, then the reaction must be first-order in A, and the value of x is 1. However, if doubling the concentration of A quadruples the rate, it is clear that [A] must have an exponent of 2, and the reaction is second-order in A. One very important point to remember is that there is no *necessary* correlation between the balancing coefficients in the chemical equation and the exponents in the rate law. They *may* be the same, but one can not *assume* that they will be without studying the rate of the reaction.

If a reaction takes place in a series of steps, a study of the rate of the reaction gives information about the slowest step of the reaction. We can

see an analogy to this in the following illustration that involves the flow of water,



If we study the rate of flow of water through this system of short pipes, information will be obtained about the flow of water through a 1" pipe since the 3" and 5" pipes do not normally offer as much resistance to flow as does the 1" pipe. Therefore, in the language of chemical kinetics, the 1" pipe represents the *rate-determining step*.

Suppose we have a chemical reaction that can be written as

$$2A + B \rightarrow \text{Products} \tag{1.5}$$

and let us also suppose that the reaction takes place in steps that can be written as

$$A + B \rightarrow C \text{ (slow)} \tag{1.6}$$

$$C + A \rightarrow \text{Products (fast)} \tag{1.7}$$

The amount of C (known as an *intermediate*) that is present at any time limits the rate of the overall reaction. Note that the sum of Eqs. (1.6) and (1.7) gives the overall reaction that was shown in Eq. (1.5). Note also that the formation of C depends on the reaction of one molecule of A and one of B. That process will likely have a rate that depends on $[A]^1$ and $[B]^1$. Therefore, even though the balanced overall equation involves *two* molecules of A, the *slow step* involves only one molecule of A. As a result, formation of products follows a rate law that is of the form Rate $= k[A][B]$, and the reaction is second-order (first-order in A and first-order in B). It should be apparent that we can write the rate law directly from the balanced equation only if the reaction takes place in a *single step*. If the reaction takes place in a series of steps, a rate study will give information about steps up to and including the slowest step, and the rate law will be determined by that step.

1.2 DEPENDENCE OF RATES ON CONCENTRATION

In this section, we will examine the details of some rate laws that depend on the concentration of reactants in some simple way. Although many

complicated cases are well known (see Chapter 2), there are also a great many reactions for which the dependence on concentration is first-order, second-order, or zero-order.

1.2.1 First-Order

Suppose a reaction can be written as

$$A \rightarrow B \tag{1.8}$$

and that the reaction follows a rate law of the form

$$\text{Rate} = k[A]^1 = -\frac{d[A]}{dt} \tag{1.9}$$

This equation can be rearranged to give

$$-\frac{d[A]}{[A]} = k\ dt \tag{1.10}$$

Equation (1.10) can be integrated but it should be integrated between the limits of time = 0 and time equal to t while the concentration varies from the initial concentration $[A]_o$ at time zero to [A] at the later time. This can be shown as

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = k\int_0^t dt \tag{1.11}$$

When the integration is performed, we obtain

$$\ln\frac{[A]_o}{[A]} = kt \quad \text{or} \quad \log\frac{[A]_o}{[A]} = \frac{k}{2.303}t \tag{1.12}$$

If the equation involving natural logarithms is considered, it can be written in the form

$$\ln [A]_o - \ln [A] = kt \tag{1.13}$$

or

$$\begin{aligned} \ln [A] &= \ln [A]_o - kt \\ y &= b + mx \end{aligned} \tag{1.14}$$

It must be remembered that $[A]_o$, the initial concentration of A, has some fixed value so it is a constant. Therefore, Eq. (1.14) can be put in the

form of a linear equation where $y = \ln[A]$, $m = -k$, and $b = \ln [A]_o$. A graph of ln[A] versus t will be linear with a slope of $-k$. In order to test this rate law, it is necessary to have data for the reaction which consists of the concentration of A determined as a function of time. This suggests that in order to determine the concentration of some species, in this case A, simple, reliable, and rapid analytical methods are usually sought. Additionally, one must measure time, which is not usually a problem unless the reaction is a very rapid one.

It may be possible for the concentration of a reactant or product to be determined directly within the reaction mixture, but in other cases a sample must be removed for the analysis to be completed. The time necessary to remove a sample from the reaction mixture is usually negligibly short compared to the reaction time being measured. What is usually done for a reaction carried out in solution is to set up the reaction in a vessel that is held in a constant temperature bath so that fluctuations in temperature will not cause changes in the rate of the reaction. Then the reaction is started, and the concentration of the reactant (A in this case) is determined at selected times so that a graph of ln[A] versus time can be made or the data analyzed numerically. If a linear relationship provides the best fit to the data, it is concluded that the reaction obeys a first-order rate law. Graphical representation of this rate law is shown in Figure 1.2 for an initial concentration of A of 1.00 **M** and $k = 0.020\,\text{min}^{-1}$. In this case, the slope of the line is $-k$, so the kinetic data can be used to determine k graphically or by means of linear regression using numerical methods to determine the slope of the line.

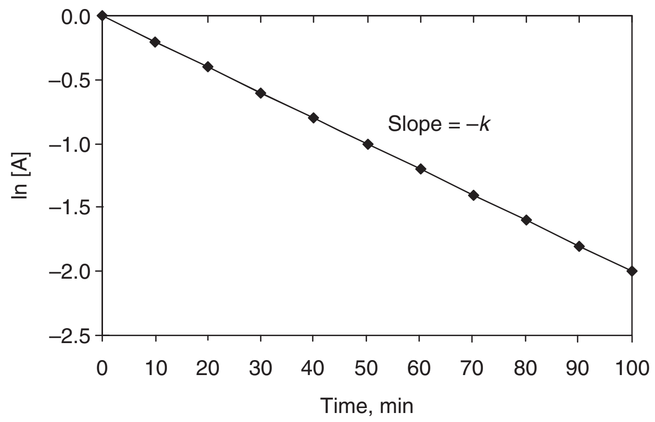


FIGURE 1.2 First-order plot for A → B with $[A]_o = 1.00\,\mathbf{M}$ and $k = 0.020\,\text{min}^{-1}$.

The units on k in the first-order rate law are in terms of time^{-1}. The left-hand side of Eq. (1.12) has [concentration]/[concentration], which causes the units to cancel. However, the right-hand side of the equation will be dimensionally correct only if k has the units of time^{-1}, because only then will kt have no units.

The equation

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_{\mathrm{o}} - kt \tag{1.15}$$

can also be written in the form

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{o}}\, \mathrm{e}^{-kt} \tag{1.16}$$

From this equation, it can be seen that the concentration of A decreases with time in an exponential way. Such a relationship is sometimes referred to as an *exponential decay*.

Radioactive decay processes follow a first-order rate law. The rate of decay is proportional to the amount of material present, so doubling the amount of radioactive material doubles the measured counting rate of decay products. When the amount of material remaining is one-half of the original amount, the time expired is called the *half-life*. We can calculate the half-life easily using Eq. (1.12). At the point where the time elapsed is equal to one half-life, $t = t_{1/2}$, the concentration of A is one-half the initial concentration or $[\mathrm{A}]_{\mathrm{o}}/2$. Therefore, we can write

$$\ln\frac{[\mathrm{A}]_{\mathrm{o}}}{[\mathrm{A}]} = \ln\frac{[\mathrm{A}]_{\mathrm{o}}}{\dfrac{[\mathrm{A}]_{\mathrm{o}}}{2}} = kt_{1/2} = \ln 2 = 0.693 \tag{1.17}$$

The half-life is then given as

$$t_{1/2} = \frac{0.693}{k} \tag{1.18}$$

and it will have units that depend on the units on k. For example, if k is in hr^{-1}, then the half-life will be given in hours, etc. Note that for a process that follows a first-order rate law, the half-life is independent of the initial concentration of the reactant. For example, in radioactive decay the half-life is independent of the amount of starting nuclide. This means that if a sample initially contains 1000 atoms of radioactive material, the half-life is exactly the same as when there are 5000 atoms initially present.

It is easy to see that after one half-life the amount of material remaining is one-half of the original; after two half-lives, the amount remaining is one-fourth of the original; after three half-lives, the amount remaining

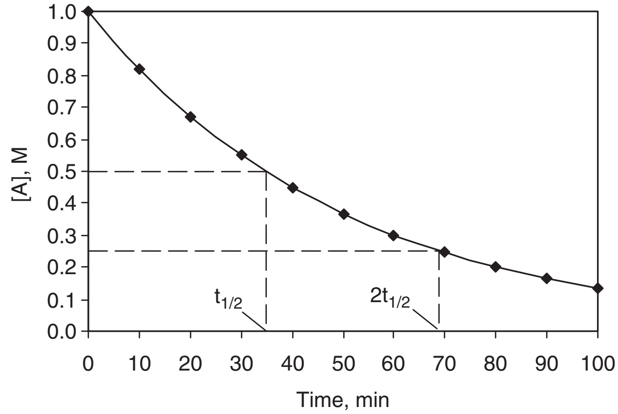


FIGURE 1.3 Half-life determination for a first-order process with $[A]_o = 1.00\,\mathbf{M}$ and $k = 0.020\,\text{min}^{-1}$.

is one-eighth of the original, etc. This is illustrated graphically as shown in Figure 1.3.

While the term *half-life* might more commonly be applied to processes involving radioactivity, it is just as appropriate to speak of the half-life of a chemical reaction as the time necessary for the concentration of some reactant to fall to one-half of its initial value. We will have occasion to return to this point.

1.2.2 Second-Order

A reaction that is second-order in one reactant or component obeys the rate law

$$\text{Rate} = k[\text{A}]^2 = -\frac{d[\text{A}]}{dt} \tag{1.19}$$

Such a rate law *might* result from a reaction that can be written as

$$2\ \text{A} \rightarrow \ \text{Products} \tag{1.20}$$

However, as we have seen, the rate law cannot always be written from the balanced equation for the reaction. If we rearrange Eq. (1.19), we have

$$\frac{-d[\text{A}]}{[\text{A}]^2} = k\ dt \tag{1.21}$$

If the equation is integrated between limits on concentration of $[A]_o$ at $t = 0$ and [A] at time t, we have

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = k \int_0^t dt \tag{1.22}$$

Performing the integration gives the integrated rate law

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \tag{1.23}$$

Since the initial concentration of A is a constant, the equation can be put in the form of a linear equation,

$$\begin{aligned} \frac{1}{[A]} &= kt + \frac{1}{[A]_o} \\ y &= mx + b \end{aligned} \tag{1.24}$$

As shown in Figure 1.4, a plot of 1/[A] versus time should be a straight line with a slope of k and an intercept of $1/[A]_o$ if the reaction follows the second-order rate law. The units on each side of Eq. (1.24) must be 1/concentration. If concentration is expressed in mole/liter, then 1/concentration will have units of liter/mole. From this we find that the units on k must be liter/mole time or $\mathbf{M}^{-1}$ time^{-1} so that kt will have units M^{-1}.

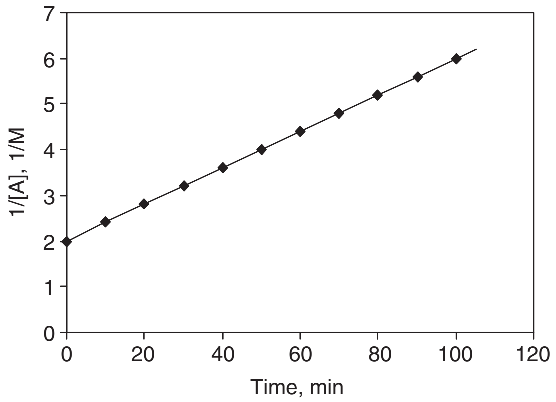


FIGURE 1.4 A second-order rate plot for A → B with $[A]_o = 0.50\,\mathbf{M}$ and $k = 0.040$ liter/mol min.

The half-life for a reaction that follows a second-order rate law can be easily calculated. After a reaction time equal to one half-life, the concentration of A will have decreased to one-half its original value. That is, $[A] = [A]_o/2$, so this value can be substituted for [A] in Eq. (1.23) to give

$$\frac{1}{\frac{[A]_o}{2}} - \frac{1}{[A]_o} = kt_{1/2} \tag{1.25}$$

Removing the complex fraction gives

$$\frac{2}{[A]_o} - \frac{1}{[A]_o} = kt_{1/2} = \frac{1}{[A]_o} \tag{1.26}$$

Therefore, solving for $t_{1/2}$ gives

$$t_{1/2} = \frac{1}{k[A]_o} \tag{1.27}$$

Here we see a major difference between a reaction that follows a second-order rate law and one that follows a first-order rate law. For a first-order reaction, the half-life is independent of the initial concentration of the reactant, but in the case of a second-order reaction, the half-life is inversely proportional to the initial concentration of the reactant.

1.2.3 Zero-Order

For certain reactions that involve one reactant, the rate is independent of the concentration of the reactant over a wide range of concentrations. For example, the decomposition of hypochlorite on a cobalt oxide catalyst behaves this way. The reaction is

$$2\ OCl^- \xrightarrow{\text{catalyst}} 2\ Cl^- + O_2 \tag{1.28}$$

The cobalt oxide catalyst forms when a solution containing Co^{2+} is added to the solution containing OCl^-. It is likely that some of the cobalt is also oxidized to Co^{3+}, so we will write the catalyst as Co_2O_3, even though it is probably a mixture of CoO and Co_2O_3.

The reaction takes place on the active portions of the surface of the solid particles of the catalyst. This happens because OCl^- is adsorbed to the solid, and the surface becomes essentially covered or at least the active sites do. Thus, the *total* concentration of OCl^- in the solution does not matter as long as there is enough to cover the active sites on the surface of the

catalyst. What *does* matter in this case is the surface area of the catalyst. As a result, the decomposition of OCl^- on a specific, fixed amount of catalyst occurs at a constant rate over a wide range of OCl^- concentrations. This is not true as the reaction approaches completion, and under such conditions the concentration of OCl^- does affect the rate of the reaction because the concentration of OCl^- determines the rate at which the active sites on the solid become occupied.

For a reaction in which a reactant disappears in a zero-order process, we can write

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^0 = k \tag{1.29}$$

because $[\mathrm{A}]^0 = 1$. Therefore, we can write the equation as

$$-d[\mathrm{A}] = k\ dt \tag{1.30}$$

so that the rate law in integral form becomes

$$-\int_{[\mathrm{A}]_o}^{[\mathrm{A}]} d[\mathrm{A}] = k\int_0^t dt \tag{1.31}$$

Integration of this equation between the limits of $[\mathrm{A}]_o$ at zero time and [A] at some later time, t, gives

$$[\mathrm{A}] = [\mathrm{A}]_o - kt \tag{1.32}$$

This equation indicates that at any time after the reaction starts, the concentration of A is the initial value minus a constant times t. This equation can be put in the linear form

$$\begin{aligned} [\mathrm{A}] &= -k \cdot t + [\mathrm{A}]_o \\ y &= m \cdot x + b \end{aligned} \tag{1.33}$$

which shows that a plot of [A] versus time should be linear with a slope of $-k$ and an intercept of $[\mathrm{A}]_o$. Figure 1.5 shows such a graph for a process that follows a zero-order rate law, and the slope of the line is $-k$, which has the units of **M** time^{-1}.

As in the previous cases, we can determine the half-life of the reaction because after one half-life, $[\mathrm{A}] = [\mathrm{A}]_o/2$. Therefore,

$$\frac{[\mathrm{A}]_o}{2} = [\mathrm{A}]_o - kt_{1/2} \tag{1.34}$$

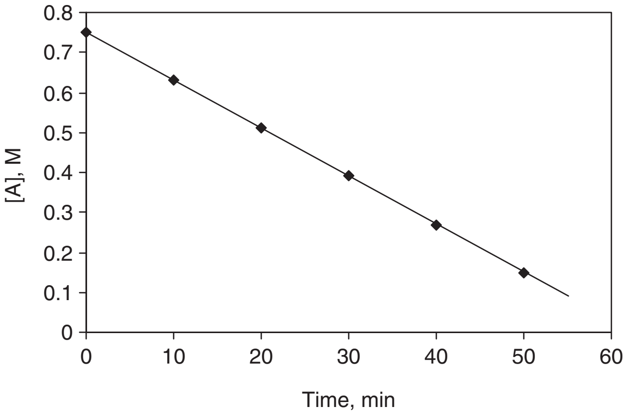


FIGURE 1.5 A zero-order rate plot for a reaction where $[A]_o = 0.75\,\mathbf{M}$ and k = 0.012 mol/l.

so that

$$t_{1/2} = \frac{[A]_o}{2k} \tag{1.35}$$

In this case, we see that the half-life is directly proportional to $[A]_o$, the initial concentration of A.

Although this type of rate law is not especially common, it is followed by some reactions, usually ones in which some other factor governs the rate. This the case for the decomposition of OCl^- described earlier. An important point to remember for this type of reaction is that eventually the concentration of OCl^- becomes low enough that there is not a sufficient amount to replace quickly that which reacts on the surface of the catalyst. Therefore, the concentration of OCl^- does limit the rate of reaction in that situation, and the reaction is no longer independent of $[OCl^-]$. The rate of reaction is independent of $[OCl^-]$ over a wide range of concentrations, but it is not *totally* independent of $[OCl^-]$. Therefore, the reaction is not strictly zero-order, but it appears to be so because there is more than enough OCl^- in the solution to saturate the active sites. Such a reaction is said to be *pseudo zero-order*. This situation is similar to reactions in aqueous solutions in which we treat the concentration of water as being a constant even though a negligible amount of it reacts. We can treat the concentration as being constant because the amount reacting compared to the amount present is very small. We will describe other pseudo-order processes in later sections of this book.

1.2.4 *N*th-Order Reaction

If a reaction takes place for which only one reactant is involved, a general rate law can be written as

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n \tag{1.36}$$

If the reaction is not first-order so that n is not equal to 1, integration of this equation gives

$$\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_{\mathrm{o}}^{\,n-1}} = (n-1)kt \tag{1.37}$$

From this equation, it is easy to show that the half-life can be written as

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[\mathrm{A}]_{\mathrm{o}}^{\,n-1}} \tag{1.38}$$

In this case, n may have either a fraction or integer value.

1.3 CAUTIONS ON TREATING KINETIC DATA

It is important to realize that when graphs are made or numerical analysis is performed to fit data to the rate laws, the points are not without some experimental error in concentration, time, and temperature. Typically, the larger part of the error is in the analytical determination of concentration, and a smaller part is in the measurement of time. Usually, the reaction temperature does not vary enough to introduce a significant error in a given kinetic run. In some cases, such as reactions in solids, it is often difficult to determine the extent of reaction (which is analogous to concentration) with high accuracy.

In order to illustrate how some numerical factors can affect the interpretation of data, consider the case illustrated in Figure 1.6. In this example, we must decide which function gives the best fit to the data. The classical method used in the past of simply inspecting the graph to see which line fits best was formerly used, but there are much more appropriate methods available. Although rapid, the visual method is not necessary today given the availability of computers. A better way is to fit the line to the points using linear regression (the method of least squares). In this method, a calculator or computer is used to calculate the sums of the squares of the deviations and then the "line" (actually a numerical relationship) is

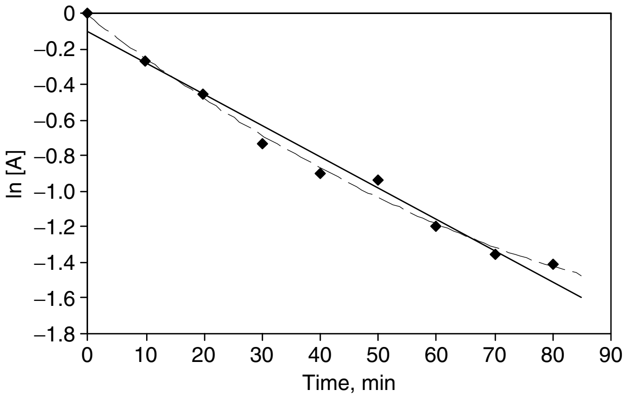


FIGURE 1.6 A plot of ln[A] versus time for data that has relatively large errors.

established, which makes these sums a minimum. This *mathematical* procedure removes the necessity for *drawing* the line at all since the slope, intercept, and correlation coefficient (a statistical measure of the "goodness" of fit of the relationship) are determined. Although specific illustrations of their use are not appropriate in this book, Excel, Mathematica, MathCad, Math lab, and other types of software can be used to analyze kinetic data according to various model systems. While the numerical procedures can remove the necessity for performing the drawing of graphs, the cautions mentioned are still necessary.

Although the preceding procedures are straightforward, there may still be some difficulties. For example, suppose that for a reaction represented as $A \rightarrow B$, we determine the following data (which are, in fact, experimental data determined for a certain reaction carried out in the solid state).

Time (min)	[A]	ln[A]
0	1.00	0.00
15	0.86	−0.151
30	0.80	−0.223
45	0.68	−0.386
60	0.57	−0.562

If we plot these data to test the zero- and first-order rate laws, we obtain the graphs shown in Figure 1.7. It is easy to see that the two graphs give about equally good fits to the data. Therefore, on the basis of the graph and the data shown earlier, it would not be possible to say unequivocally whether

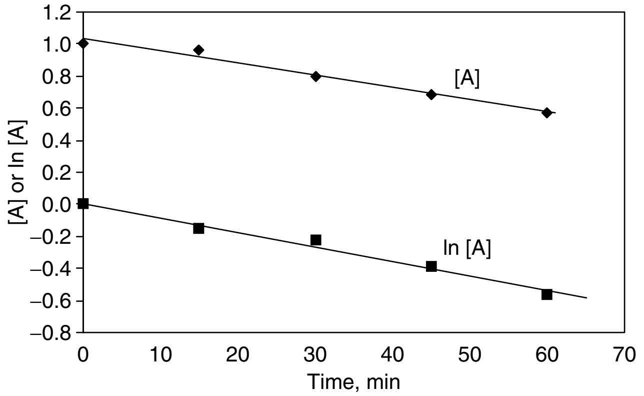


FIGURE 1.7 Rate plots for the data as described in the text.

the reaction is zero- or first-order. The fundamental problem is one of distinguishing between the two cases shown in Figure 1.7.

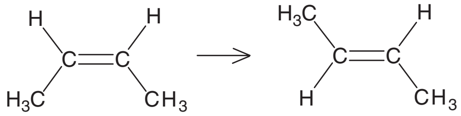
Although it might appear that simply determining the concentration of reactant more accurately would solve the problem, it may not always be possible to do this, especially for reactions in solids (see Chapter 7).

What has happened in this case is that the errors in the data points have made it impossible to decide between a line having slight curvature and one that is linear. The data that were used to construct Figure 1.7 represent a curve that shows concentration versus time in which the reaction is less than 50% complete. Within a narrow range of the concentration and the ln(concentration) variables used in zero- and first-order rate laws, respectively, almost any mathematical function will represent the curve fairly well. The way around this difficulty is to study the reaction over several half-lives so that the dependence on concentration can be determined. Only the correct rate law will represent the data when a larger extent of the reaction is considered. However, the fact remains that for some reactions it is not possible to follow the reaction that far toward completion.

In Figure 1.7, one of the functions shown represents the incorrect rate law, while the other represents the correct rate law but with rather large errors in the data. Clearly, to insure that a kinetic study is properly carried out, the experiment should be repeated several times, and it should be studied over a sufficient range of concentration so that any errors will not make it impossible to determine which rate law is the best-fitting one. After the correct rate law has been identified, several runs can be carried out so that an average value of the rate constant can be determined.

1.4 EFFECT OF TEMPERATURE

In order for molecules to be transformed from reactants to products, it is necessary that they pass through some energy state that is higher than that corresponding to either the reactants or products. For example, it might be necessary to bend or stretch some bonds in the reactant molecule before it is transformed into a product molecule. A case of this type is the conversion of *cis*–2–butene to *trans*–2–butene,



(1.39)

For this reaction to occur, there must be rotation around the double bond to such an extent that the π–bond is broken when the atomic *p*–orbitals no longer overlap.

Although other cases will be discussed in later sections, the essential idea is that a state of higher energy must be populated as a reaction occurs. This is illustrated by the energy diagram shown in Figure 1.8. Such a situation should immediately suggest that the *Boltzmann Distribution Law* may provide a basis for the explanation because that law governs the *population of states of unequal energy*. In the case illustrated in the figure, $[\ ]^{\ddagger}$ denotes the high-energy state, which is called the *transition state* or the *activated complex*. The height of the energy barrier over which the reactants must pass on the

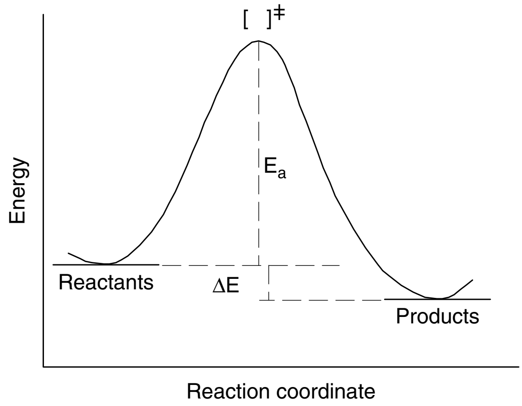


FIGURE 1.8 The energy profile for a chemical reaction.

way to becoming products is known as the *activation energy*. The example illustrated in the figure represents an exothermic reaction because the overall energy change is negative since the products have a lower energy than the reactants.

When the various rate laws are inspected, we see that only k can be a function of temperature because the concentrations remain constant or very nearly so as the temperature changes only a small amount. Therefore, it is the *rate constant* that incorporates information about the effect of *temperature* on the rate of a reaction.

There are several types of behavior exhibited when the rates of reactions are studied as a function of temperature. Three of the most common variations in rate with temperature are shown in Figure 1.9.

The first case shows the variation followed by most reactions, that of an exponentially increasing rate as temperature increases. The second shows the behavior of some material that becomes explosive at a certain temperature. At temperatures below the explosive limit, the rate is essentially unaffected by the temperature. Then, as the temperature is reached at which the material becomes explosive, the rate increases enormously as the temperature is increased only very slightly. In the third case, we see the variation in rate of reaction that is characteristic of many biological processes. For example, reactions involving enzymes (biological catalysts) frequently increase in rate up to a certain temperature and then decrease in rate at higher temperatures. Enzymes are protein materials that can change conformation or become denatured at high temperatures. Therefore, the rates of enzyme catalyzed reactions usually show that there is some optimum temperature where the rate is maximum, and the rate decreases when the temperature is above or below that temperature (see Chapter 6).

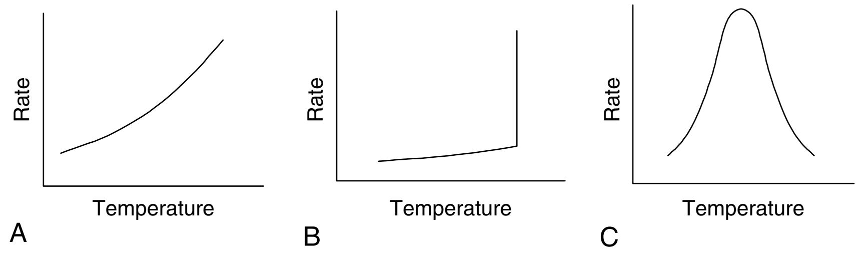


FIGURE 1.9 Some of the ways in which reaction rates vary with temperature.

Svante August Arrhenius suggested in the late 1800s that the rates of most reactions vary with temperature (as shown in Figure 1.9*a*) in such a way that

$$k = Ae^{-E_a/\mathrm{RT}} \tag{1.40}$$

where k is the rate constant, A is the *frequency factor* (or pre-exponential factor), R is the molar gas constant, E_a is the activation energy, and T is the temperature (K). This equation is generally referred to as the *Arrhenius equation*. If we take the natural logarithm of both sides of Eq. (1.40), we obtain

$$\ln k = -\frac{E_a}{\mathrm{RT}} + \ln A \tag{1.41}$$

By rearrangement, this equation can be put in the form of a straight line,

$$\begin{aligned} \ln k &= -\frac{E_a}{\mathrm{R}} \cdot \frac{1}{\mathrm{T}} + \ln A \\ y &= m \cdot x + b \end{aligned} \tag{1.42}$$

Therefore, a plot of ln k versus 1/T can be made or linear regression performed after the rate constants have been determined for a reaction carried out at several temperatures. The slope of the line is $-E_a$/R and the intercept is ln A. Such a graph, like that shown in Figure 1.10, is often called an *Arrhenius plot*. It is from the slope, determined either numerically or graphically, that the activation energy is determined.

For a particular reaction, the following rate constants were obtained when the reaction was studied at a series of temperatures which yielded the data shown on the next page.

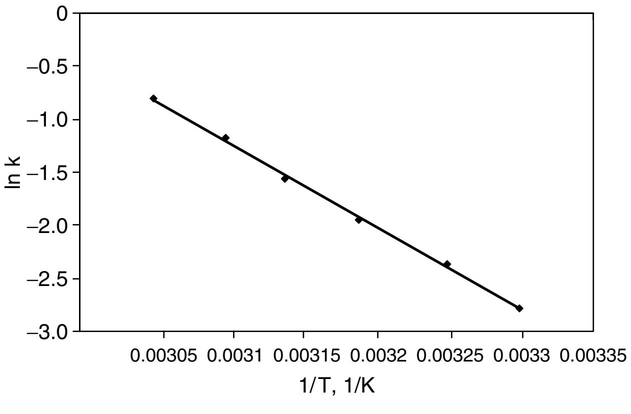


FIGURE 1.10 An Arrhenius plot constructed using the data in the text.

T, K	1/T, K^{-1}	k, sec^{-1}	ln k
30	0.00330	0.0623	−2.78
35	0.00325	0.0948	−2.36
40	0.00319	0.142	−1.95
45	0.00314	0.210	−1.56
50	0.00310	0.308	−1.18
55	0.00305	0.445	−0.809

These data were used to construct the Arrhenius plot shown in Figure 1.10. By performing linear regression on the data, the activation energy is found to be 65.0 kJ/mol and the frequency factor is 1.0×10^{10} sec^{-1}.

In determining the activation energy from an Arrhenius plot, it is important to observe several precautions. For example, if the reaction is being studied at 300 K, the value of 1/T will be 0.00333 K^{-1}. If the reaction is then studied at 305 K, the value of 1/T will be 0.00328 K^{-1}. Such small differences in 1/T make it very difficult to determine the slope of the line accurately, especially if the temperature has not been controlled *very* accurately. Consequently, it is desirable to study a reaction over as large a range of temperature as possible and to use several temperatures within that range in order to minimize errors. For most reactions, the temperature range in which the reaction can be studied is rather limited because at low temperatures the reaction will be very slow and at high temperatures the reaction will be very fast. Therefore, it is generally desired to study a reaction over a range of at least 20–25°.

If the rate constant for a reaction is determined at only two temperatures, it is still possible to evaluate the activation energy, but such a case is not nearly as desirable as the procedure described earlier. Small errors in the rate constants will cause inaccuracy in the activation energy determined, because all of the errors in placing the line are present in only two points. More data would be needed to "average out" the error in the value of any one rate constant. If k_1 is the rate constant at T_1 and k_2 is the rate constant at T_2, we can write the Arrhenius equation as

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \tag{1.43}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \tag{1.44}$$

Subtracting the equation for ln k_2 from that giving ln k_1 gives

$$\ln k_1 - \ln k_2 = \left(\ln A - \frac{E_a}{RT_1}\right) - \left(\ln A - \frac{E_a}{RT_2}\right) \tag{1.45}$$

We can simplify this equation to obtain

$$\ln\frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{RT_1T_2} \tag{1.46}$$

To carry out a very *elementary* kinetic study, the following things must be done as a minimum before the reaction can be interpreted from a kinetic viewpoint.

1. Carry out the reaction at a constant temperature and determine the concentration of a reactant or product after various time intervals.
2. Fit the data to the appropriate rate law keeping in mind that the reaction must be studied over several half-lives, and the experiment should be carried out several times.
3. Determine the rate constant at the temperature at which the reaction was studied. An average value of k from several runs is preferred.
4. After the rate law is known, study the reaction over as wide a range of temperature as possible, repeating steps 1–3. Make replicate runs at each temperature.
5. After the average rate constant is obtained at each temperature, fit the rate constants to the Arrhenius equation and determine the activation energy from the slope.

These steps constitute a simplified kinetic study, and other factors would have to be investigated in many cases. For example, the effect of changing the solvent is frequently studied if the reaction is carried out in solution. Also, the presence of materials that do not participate directly in the reaction may affect the rate of the reaction. For example, if the reaction is between ions, the ionic strength of the solution may have an effect on the rate. These and other factors may be studied in particular cases, and they will be discussed in more detail in later chapters.

1.5 SOME COMMON REACTION MECHANISMS

When using the term *mechanism* as it applies to a reaction, we mean the details of the number of molecules and their arrangement at the time the

reaction occurs. This is sometimes summarized by use of the phrase *critical configuration*. A rate law gives the *molecularity* of the reaction (the number of molecules required to form the transition state), which is usually the same as the overall order of the reaction. Frequently, other experiments are required to determine other information about the reaction. We will see examples of this when specific reactions are described in more detail.

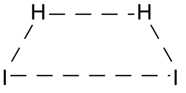
Some reactions appear to occur as a direct result of molecular collision, especially for reactions in the gas phase. However, it is not a simple matter to calculate the total number of collisions, the fraction of those collisions that have great enough energy to form the transition state that leads to products, and the fraction of the collisions that have the molecules in exactly the right orientation to react to form the transition state. As a result, reaction rates must be measured experimentally even for rather simple gaseous reactions. For reactions taking place in solutions, the factors mentioned previously are important but there are also the effects caused by the solvent. For example, if a reactant is polar or ionic, it will be strongly solvated in a polar solvent such as water or an alcohol. Also, in aqueous solutions there will be the effects of acidity or basicity to consider. Even with all of these problems, there have been so many reactions studied in sufficient detail that the mechanisms are well understood. We will now describe briefly a few of the important mechanisms that will serve as models to illustrate the general approaches used to study mechanisms, and the discussion will be amplified in later chapters.

1.5.1 Direct Combination

The reaction between $H_2(g)$ and $I_2(g)$,

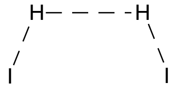
$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g) \tag{1.47}$$

has been studied by several workers over a long period of time. This reaction has been found to be first-order in both H_2 and I_2. Therefore, the transition state (or activated complex) consists of one molecule of each reactant. For many years, it was believed that the transition state had a structure like



in which the H–H and I–I bonds are breaking as the H–I bonds are being formed. However, more recent studies have shown that the I_2 molecules

may be dissociated before they react, and the transition state probably has a structure like



The rate law would still show a first-order dependence on the concentration of I_2 because the molecules dissociate to produce two I atoms,

$$I_2(g) \rightleftharpoons 2\ I\bullet\ (g) \tag{1.48}$$

Therefore, the concentration of I• depends on the concentration of I_2 so that the reaction shows a first-order dependence on $[I_2]$. As a result, the reaction follows a rate law that is first-order in both H_2 and I_2, but the nature of the transition state was misunderstood for many years. As a result, an apparently simple reaction that was used as a model in numerous chemistry texts was described incorrectly. In fact, the reaction between H_2 and I_2 *molecules* is now known to be of a type referred to as *symmetry forbidden* on the basis of orbital symmetry (see Chapter 9).

1.5.2 Chain Mechanisms

The reaction between $H_2(g)$ and $Cl_2(g)$ can be represented by the equation

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g) \tag{1.49}$$

This equation looks as simple as the one shown earlier (Eq. (1.47)) that represents the reaction between hydrogen and iodine. However, the reaction between H_2 and Cl_2 follows a completely different pathway. In this case, the reaction can be initiated by light (which has an energy expressed as $E = h\nu$). In fact, a mixture of Cl_2 and H_2 will explode if a flashbulb is fired next to a thin *plastic* container holding a mixture of the two gases. The light causes some of the Cl_2 molecules to dissociate to produce chlorine atoms (each of which has an unpaired electron and behaves as a *radical*).

$$Cl_2(g) \xrightarrow{h\nu} 2\ Cl\bullet\ (g) \tag{1.50}$$

We know that it is the Cl–Cl bond that is ruptured in this case since it is much weaker than the H–H bond (243 versus 435 kJ/mol). The next step in the process involves the reaction of Cl• with H_2.

$$Cl\bullet + H_2 \rightarrow [Cl\cdots H\cdots H] \rightarrow H\bullet + HCl \tag{1.51}$$

Then the hydrogen radicals react with Cl_2 molecules,

$$H\bullet + Cl_2 \rightarrow [H \cdots Cl \cdots Cl] \rightarrow Cl\bullet + HCl \tag{1.52}$$

These processes continue with each step generating a radical that can carry on the reaction in another step. Eventually, reactions such as

$$Cl\bullet + H\bullet \rightarrow HCl \tag{1.53}$$

$$Cl\bullet + Cl\bullet \rightarrow Cl_2 \tag{1.54}$$

$$H\bullet + H\bullet \rightarrow H_2 \tag{1.55}$$

consume radicals without forming any new ones that are necessary to cause the reaction to continue. The initial formation of Cl• as shown in Eq. (1.50) is called the *initiation* step, and the steps that form HCl and another radical are called *propagation* steps. The steps that cause radicals to be consumed without additional ones being formed are called *termination* steps. The entire process is usually referred to as a *chain* or *free-radical* mechanism, and the rate law for this multi-step process is quite complicated. Although the equation for the reaction looks as simple as that for the reaction of H_2 with I_2, the rate laws for the two reactions are quite different! These observations illustrate the fact that one cannot deduce the form of the rate law simply by looking at the equation for the overall reaction.

The reaction of H_2 with Br_2 and the reaction of Cl_2 with hydrocarbons (as well as many other reactions of organic compounds) follow chain mechanisms. Likewise, the reaction between O_2 and H_2 follows a chain mechanism. Chain mechanisms are important in numerous gas phase reactions, and they will be discussed in more detail in Chapter 4.

1.5.3 Substitution Reactions

Substitution reactions, which occur in all areas of chemistry, are those in which an atom or group of atoms is substituted for another. A Lewis base is an electron pair donor, and a Lewis acid is an electron pair acceptor. Some common Lewis bases are H_2O, NH_3, OH^-, F^-, etc., while some common Lewis acids are $AlCl_3$, BCl_3, carbocations (R_3C^+), etc. In a Lewis acid-base reaction, a *coordinate bond* is formed between the acid and base with the base donating the pair of electrons. Lewis bases are known as *nucleophiles* and Lewis acids are known as *electrophiles*. In fact, when A is a

Lewis acid and :B and :B′ are Lewis bases with B′ being the stronger base, the reaction

$$A:B + B' \rightarrow A:B' + B \tag{1.56}$$

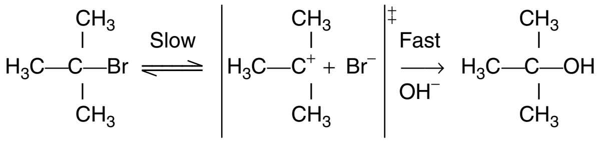
is an example of a Lewis acid-base reaction. As shown in this reaction, it is generally the stronger base that displaces a weaker one. This reaction is an example of *nucleophilic* substitution.

A nucleophilic substitution reaction that is very well known is that of tertiary butyl bromide, $t-(CH_3)_3CBr$, with hydroxide ion.

$$t-(CH_3)_3CBr + OH^- \rightarrow t-(CH_3)_3COH + Br^- \tag{1.57}$$

We can imagine this reaction as taking place in the two different ways that follow.

Case I. In this process, we will assume that Br^- leaves the $t-(CH_3)_3CBr$ molecule *before* the OH^- attaches which is shown as



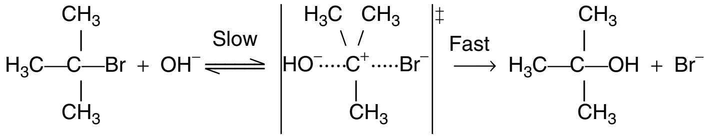
(1.58)

where [ ]‡ denotes the transition state, which in this case contains two ions. One of these contains a carbon atom having a positive charge, a species referred to as a *carbocation* (also sometimes called a *carbonium* ion). The formation of $t\text{–}(CH_3)_3^+$ and Br^- requires the C–Br bond to be broken, which is the slow step and thus rate determining. In this case, the transition state involves only one molecule of $t\text{–}(CH_3)_3CBr$, and the rate law is

$$\text{Rate} = k[t\text{–}(CH_3)_3CBr] \tag{1.59}$$

If the reaction takes place by this pathway, it will be independent of OH^- concentration and follow the rate law shown in Eq. (1.59).

Case II. A second possible pathway for this reaction is one in which the OH^- starts to enter before the Br^- has completely left the $t\text{–}(CH_3)_3CBr$ molecule. In this pathway, the slow step involves the formation of a transition state that involves *both* $t\text{–}(CH_3)_3CBr$ and OH^-. The mechanism can be shown as



(1.60)

In this case, the formation of the transition state requires a molecule of $t-(CH_3)_3CBr$ and an OH^- ion in the rate-determining step, so the rate law is

$$\text{Rate} = k[t-(CH_3)_3CBr][OH^-] \tag{1.61}$$

When the reaction

$$t-(CH_3)_3CBr + OH^- \rightarrow t-(CH_3)_3COH + Br^- \tag{1.62}$$

is studied in basic solutions, the rate is found to be independent of OH^- concentration over a rather wide range. Therefore, under these conditions, the reaction occurs by the pathway shown in Case I. This process is referred to as a *dissociative* pathway because it depends on the dissociation of the C–Br bond in the rate-determining step. Since the reaction is a nucleophilic substitution and it is first-order, it is also called an S_N1 process.

The fact that the reaction in basic solutions is observed to be first-order indicates that the slow step involves only a molecule of $t-(CH_3)_3CBr$. The second step, the addition of OH^- to the $t-(CH_3)_3C^+$ carbocation, is fast *under these conditions*. At low concentrations of OH^-, the second step in the process shown in Case I may *not* be fast compared to the first. The reason for this is found in the Boltzmann Distribution Law. The transition state represents a high-energy state populated according to a Boltzmann distribution. If a transition state were to be 50 kJ/mol higher in energy than the reactant state, the relative populations at 300 K would be

$$\frac{n_2}{n_1} = e^{-E/RT} = e^{-50,000/8.3144\times300} = 2 \times 10^{-9} \tag{1.63}$$

if no other factors (such as solvation) were involved. Therefore, if the reactants represent a 1.0 **M** concentration, the transition state would be present at a concentration of 2×10^{-9} **M**. In a basic solution having a pH of 12.3, the $[OH^-]$ is 2×10^{-2} **M** so there will be about 10^7 OH^- ions for every $t-(CH_3)_3C^+$! It is not surprising that the second step in the process represented by Case I is fast when there is such an enormous excess of OH^- compared to $t-(CH_3)_3C^+$. On the other hand, at a pH of 5.0, the OH^- concentration is 10^{-9} **M**, and the kinetics of the reaction is decidedly different. Under these conditions, the second step is no longer very fast compared to the first, and the rate law now depends on $[OH^-]$ as well. Therefore, at low OH^- concentrations, the reaction follows a second-order rate law, first-order in both $t-(CH_3)_3CBr$ and OH^-.

Since the reaction described involves *two* reacting species, there must be *some* conditions under which the reaction is *second-order*. The reason it

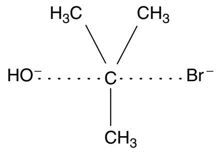
appears to be first-order at all is because of the relatively large concentration of OH^- compared to the concentration of the carbocation in the transition state. The reaction is in reality a *pseudo first-order* reaction in basic solutions.

Another interesting facet of this reaction is revealed by examining the transition state in the first-order process (Case I). In that case, the transition state consists of two *ions*. Because the reaction as described is being carried out in an aqueous solution, these ions will be strongly solvated as a result of ion-dipole forces. Therefore, part of the energy required to break the C–Br bond will be recovered from the solvation enthalpies of the ions that are formed in the transition state. This is often referred to as *solvent-assisted transition state formation*. It is generally true that the formation of a transition state in which charges are separated is favored by carrying out the reaction in a polar solvent that solvates the charged species (this will be discussed more fully in Chapter 5).

If the reaction

$$t\text{–}(CH_3)_3CBr + OH^- \rightarrow t\text{–}(CH_3)_3COH + Br^- \quad (1.64)$$

is carried out in a solvent such as methanol, CH_3OH, it follows a second-order rate law. In this case, the solvent is not as effective in solvating ions as is H_2O (largely because of the differences in polarity and size of the molecules) so that the charges do not separate completely to form an *ionic* transition state. Instead, the transition state indicated in Case II forms



and it requires *both* $t\text{–}(CH_3)_3CBr$ and OH^- for its formation. As a result, when methanol is the solvent, the rate law is

$$\text{Rate} = k[t\text{–}(CH_3)_3CBr][OH^-] \quad (1.65)$$

In this case, two species become *associated* during the formation of the transition state so this pathway is called an *associative* pathway. Because the reaction is a nucleophilic substitution that follows a second-order rate law, it is denoted as an S_N2 reaction.

If the reaction is carried out in a suitable mixture of CH_3OH and H_2O, the observed rate law is

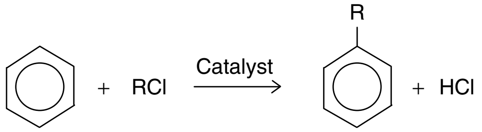
$$\text{Rate} = k_1[t\text{–}(CH_3)_3CBr] + k_2[t\text{–}(CH_3)_3CBr][OH^-] \quad (1.66)$$

indicating that both S_N1 (dissociative) and S_N2 (associative) pathways are being followed.

1.6 CATALYSIS

If there is a topic that is important to all branches of chemistry, it is catalysis. The gasoline used as fuel, the polymers used in fabrics, the sulfuric acid used in an enormous range of chemical processes, and the ammonia used as fertilizer are all produced by catalyzed reactions. In addition, many biological reactions are catalyzed by materials known as enzymes. As a result, it would be hard to overemphasize the importance of catalysis. In this section, we will describe some processes in which catalysts play an important role.

One of the important processes in organic chemistry is the reaction in which an alkyl group is attached to benzene. This reaction, known as the Friedel-Crafts reaction, can be shown as



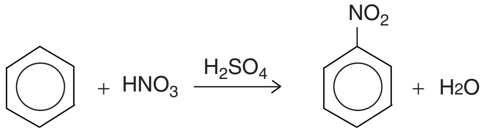
(1.67)

where R is an alkyl group (CH_3, C_2H_5, etc.). The catalyst normally used in this reaction is $AlCl_3$, although other catalysts can also be used. This reaction involves the interaction between $AlCl_3$ and RCl to produce R^+,

$$AlCl_3 + RCl \rightleftharpoons AlCl_4^- + R^+ \tag{1.68}$$

which occurs because $AlCl_3$ is a strong Lewis acid that has a great affinity for Cl^-. Therefore, it interacts with an unshared pair of electrons on the Cl in the RCl molecule to cause it to be removed from the alkyl group. The R^+ then attacks the benzene ring to yield the final product, C_6H_5R. The function of the *acid* catalyst is to produce a *positive* species, which then attacks the other reactant. Acylation reactions can also be carried out using RCOCl and $AlCl_3$ because $AlCl_3$ removes a chloride ion from the acyl halide which generates RCO^+, a positive attacking species.

Another reaction of this type is that in which an NO_2 group is introduced into an organic molecule. An example of this process is

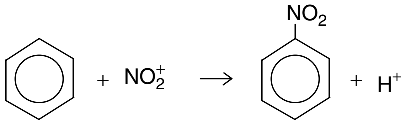


(1.69)

In this case, the function of the H_2SO_4 is to protonate some of the HNO_3, which in turn leads to some NO_2^+ being produced by the process

$$HNO_3 + H_2SO_4 \rightleftharpoons HSO_4^- + H_2NO_3^+ \rightarrow NO_2^+ + H_2O \qquad (1.70)$$

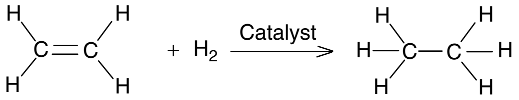
The NO_2^+, known as the *nitronium* ion, attacks the benzene ring to form the product, nitrobenzene.



(1.71)

The *acid* catalyst, H_2SO_4, functions to generate a *positive* attacking species, which is generally the function of an acid catalyst. While we will not show specific examples here, it is the function of a *base* catalyst to generate a *negative* attacking species.

Hydrogenation reactions are reactions in which hydrogen is added to some compound, particularly unsaturated organic compounds. A large number of reactions of this type are of commercial importance, and almost all of them are catalyzed by either a solid catalyst (heterogeneous catalysis) or some catalyst in solution (homogeneous catalysis). One of the simplest reactions of this type is the hydrogenation of ethylene to produce ethane.



(1.72)

In this case, the catalyst is usually a metal such as platinum or nickel, and the function of the catalyst is of considerable interest. In order to understand how the catalyst works, it is necessary to know how hydrogen interacts with metals.

We can picture a metal as being made up of spherical atoms in a close packing arrangement with a surface layer of atoms having a structure similar to that shown in Figure 1.11. This figure also shows H and C_2H_4 adsorbed at active sites on the metal surface. In the process of adsorbing H_2 on the surface of the metal, some of the molecules become dissociated or at least the H–H bonds are weakened. Also, because the metals that catalyze hydrogenation reactions are those which form interstitial hydrides, some of the hydrogen penetrates to interstitial positions in the metal, which also favors the dissociation of H_2 molecules. Both of these processes produce some reactive hydrogen atoms that can react with ethylene when it is also adsorbed on the surface of the metal. The details of the hydrogenation are

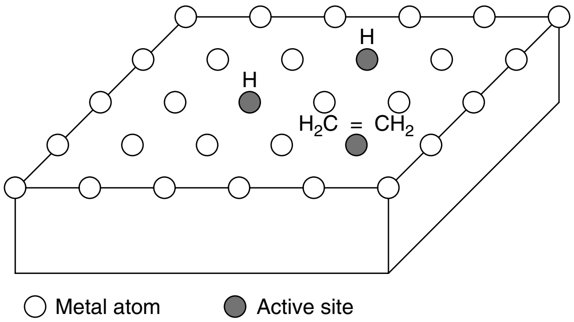


FIGURE 1.11 The surface of a metal catalyst with gases adsorbed on active sites.

not completely understood, but the adsorption of H_2 and C_2H_4 is undoubtedly involved. Adsorption and dissolution of H_2 in the metal both favor the separation of the molecules, and the reactive H atoms then react with the double bond in $H_2C = CH_2$, which subsequently leaves the surface of the metal as a molecule of C_2H_6.

Many reactions that are catalyzed by a solid in a process that is heterogeneous have as the essential step the *adsorption* of the reactants on the solid surface. The preparation of catalysts having surface characteristics that make them more effective in this type of interaction is currently a very important area of chemistry. In the *cracking* of hydrocarbons as represented by the equation

$$RCH_2CH_2R' \xrightarrow[500^\circ C,\, 2\,atm]{Catalyst} RH + R'CH = CH_2 \tag{1.73}$$

the catalyst is usually a mixture of SiO_2 and Al_2O_3 in the form of a finely divided amorphous gel. The surface area of this type of material may be as high as $500\ m^2/g$, and the active sites behave as Lewis acids. Eventually, the surface of the catalyst becomes partially covered with carbon, and it must be regenerated thermally. This process causes loss of some of the surface area by rounding and smoothing of the particles as they attempt to form a smaller surface area to minimize the number of units (which may be atoms, molecules, or ions, depending on the type of solid) on the surface. This motion of units of a solid to form a smaller surface area is known as *sintering*. The units on the surface of a solid are not surrounded equally on all sides by other units so they are subjected to unbalanced forces. A lower energy is achieved when the number of surface units is reduced, and this is achieved by rounding the surface because a given volume of material has

the smallest surface area when it has a spherical shape. Developed in the 1930s, the cracking processes produce some low molecular weight products such as ethylene, propylene, and butenes, which are also useful in the preparation of polymers such as polyethylene, polypropylene, etc.

Another important process involving hydrocarbons is *reforming*. This type of process involves restructuring molecules so that they function better for some particular use, such as motor fuels. The early catalysts for this type of process were Al_2O_3 containing some Cr_2O_3 or Mo_2O_3, but a platinum catalyst is now more widely used. Typical reactions of this type are the following.

$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Catalyst}} C_6H_{12} + H_2 \tag{1.74}$$

$$C_6H_{12} \rightarrow C_6H_6 + 3\ H_2 \tag{1.75}$$

The benzene produced by the reaction shown in Eq. (1.75) is used as a solvent, in the preparation of styrene ($C_6H_5CH = CH_2$) and in many other applications. While a comprehensive description of catalysis is beyond the scope of this chapter, it is, however, a topic of enormous importance in modern chemistry, and it will be discussed in more detail in Chapters 4 and 6.

This chapter provides a review of some of the topics that are usually covered in earlier chemistry courses and presents an introduction to several of the topics that will be treated in more detail in subsequent chapters. We will begin the more detailed study of kinetics in the next chapter by considering the treatment of systems that follow more complicated rate laws.

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PROBLEMS

1. For the reaction A $\rightarrow$ products, the following data were obtained.

Time, hrs	[A], **M**	Time, hrs	[A], **M**
0	1.24	6	0.442
1	0.960	7	0.402
2	0.775	8	0.365
3	0.655	9	0.335
4	0.560	10	0.310
5	0.502		

   (a) Make appropriate plots or perform linear regression using these data to test them for fitting zero-, first-, and second-order rate laws. Test all three even if you happen to guess the correct rate law on the first trial. (b) Determine the rate constant for the reaction. (c) Using the rate law that you have determined, calculate the half-life for the reaction. (d) At what time will the concentration of A be 0.380?

2. For the reaction X $\rightarrow$ Y, the following data were obtained.

Time, min	[X], **M**	Time, min	[X], **M**
0	0.500	60	0.240
10	0.443	70	0.212
20	0.395	80	0.190
30	0.348	90	0.171
40	0.310	100	0.164
50	0.274		

   (a) Make appropriate plots or perform linear regression using these data to determine the reaction order. (b) Determine the rate constant for the reaction. (c) Using the rate law you have determined, calculate

the half-life for the reaction. (d) Calculate how long it will take for the concentration of X to be 0.330 **M**.

3. If the half-life for the reaction

$$C_2H_5Cl \rightarrow C_2H_4 + HCl$$

is the same when the initial concentration of C_2H_5Cl is 0.0050 *M* and 0.0078 **M**, what is the rate law for this reaction?

4. When the reaction A + 2B → D is studied kinetically, it is found that the rate law is $R = k[A][B]$. Propose a mechanism that is consistent with this observation. Explain how the proposed mechanism is consistent with the rate law.

5. The decomposition of A to produce B can be written as A → B. (a) When the initial concentration of A is 0.012 **M**, the rate is 0.0018 M min^{-1} and when the initial concentration of A is 0.024 **M**, the rate is 0.0036 M min^{-1}. Write the rate law for the reaction. (b) If the activation energy for the reaction is 268 kJ mol^{-1} and the rate constant at 660 K is 8.1×10^{-3} sec^{-1} what will be the rate constant at 690 K?

6. The rate constant for the decomposition of $N_2O_5(g)$ at a certain temperature is 1.70×10^{-5} sec^{-1}.

   (a) If the initial concentration of N_2O_5 is 0.200 mol/l, how long will it take for the concentration to fall to 0.175 mol/l?
   (b) What will be the concentration of N_2O_5 be after 16 hours of reaction?

7. Suppose a reaction has a rate constant of 0.240×10^{-3} sec^{-1} at 0 °C and 2.65×10^{-3} sec^{-1} at 24 °C. What is the activation energy for the reaction?

8. For the reaction $3\ H_2(g) + N_2(g) \rightarrow 2\ NH_3(g)$ the rate can be expressed in three ways. Write the rate expressions.

9. The reaction $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ is first-order in SO_2Cl_2. At a constant temperature the rate constant is 1.60×10^{-5} sec^{-1}. What is the half-life for the disappearance of SO_2Cl_2? After 15.0 hours, what fraction of the initial SO_2Cl_2 remains?

10. For the reaction X $\rightleftharpoons$ Y, the following data were obtained for the forward (k_f) and reverse (k_r) reactions.

T, K	400	410	420	430	440
k_f, sec^{-1}	0.161	0.279	0.470	0.775	1.249
$10^3 \times k_r$, sec^{-1}	0.159	0.327	0.649	1.25	2.323

Use these data to determine the activation energy for the forward and reverse reactions.
Draw a reaction energy profile for the reaction.

11. For a reaction A $\rightarrow$ B, the following data were collected when a kinetic study was carried out at several temperatures between 25 and 45°C.

[A], **M**

t, min	T = 25°C	T = 30°C	T = 35°C	T = 40°C	T = 45°C
0	0.750	0.750	0.750	0.750	0.750
15	0.648	0.622	0.590	0.556	0.520
30	0.562	0.530	0.490	0.440	0.400
45	0.514	0.467	0.410	0.365	0.324
60	0.460	0.410	0.365	0.315	0.270
75	0.414	0.378	0.315	0.275	0.235
90	0.385	0.336	0.290	0.243	0.205

(a) Use one of the data sets and make appropriate plots or perform linear regression to determine the order of the reaction. (b) After you have determined the correct rate law, determine graphically the rate constant at each temperature. (c) Having determined the rate constants at several temperatures, determine the activation energy.

12. Suppose a solid metal catalyst has a surface area of 1000 cm^2. (a) If the distance between atomic centers is 145 pm and the structure of the metal is simple cubic, how many metal atoms are exposed on the surface? (b) Assuming that the number of active sites on the metal has an equilibrium concentration of adsorbed gas, A, and that the rate of the reaction A $\rightarrow$ B is 1.00 $\times$ 10^6 mole/sec, what fraction of the metal atoms on the surface have a molecule of A adsorbed? Assume each molecule is absorbed for 0.1 sec before reacting.

13. A reaction has a rate constant of 0.264 $\mathbf{M}^{-1}$ sec^{-1} at 45.6°C and 0.833 $\mathbf{M}^{-1}$ sec^{-1} at 58.8°C. What is the activation energy for the reaction?

14. The rate constant for a reaction is 0.322 min^{-1} at 33.0°C and the activation energy is 58.8 kJ mol^{-1}. What will be the rate constant at 70°C?

15. For a certain reaction, the rate constant varies with temperature as follows:

T, K	298	308	318	328	338
$10^3 \times k$, sec^{-1}	0.0110	0.0367	0.114	0.327	0.891

Determine the value of E_a and A for this reaction.

16. What is the activation energy for a reaction whose rate doubles when the temperature is raised from 25°C to 40°C? If the rate constant at 40°C is 2.62×10^{-4} sec^{-1}, what will be the half-life of this reaction at 35°C?

17. When initially present at 1.00 **M** concentration, one-tenth of a sample reacts in 36 minutes. (a) What is the half-life of the material if the reaction is first-order? (b) What is the half-life if the reaction is second-order?

18. The rate constants for a particular reaction vary with temperature as follows:

t,°C	25	35	45	55	65
$10^5 \times k$, sec^{-1}	1.70	6.90	24.7	78.1	245

Determine the activation energy and pre-exponential factor for this reaction.

19. Strontium-83 has a half-life of 32.4 hours. If you receive a sample of pure ^{83}Sr and must complete a study of the nuclide before 3.00% of the material decays, how long do you have to complete the required study?

20. Show that the half-life for an *n*th order reaction can be written as

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[\mathrm{A}]_{\mathrm{o}}^{\,n-1}}$$

21. For the reaction

$$\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H}$$

the values for ln$A$ and E_a are 10.9 l/mol sec and 23 kJ/mol, respectively. Determine the rate constant for this reaction at 60°C.

CHAPTER 2

Kinetics of More Complex Systems

In Chapter 1, some of the basic principles of chemical kinetics were illustrated by showing the mathematical treatment of simple systems in which the rate law is a function of the concentration of only one reactant. In many reactions, an intermediate may be formed before the product is obtained, and in other cases more than one product may be formed. The mathematical analysis of the kinetics of these processes is more complex than that for the simple systems described in Chapter 1. Because reactions of these types are both important and common, it is necessary that the mathematical procedures for analyzing the kinetics of these types of reactions be developed. Consequently, kinetic analysis of several types of complex processes will be described in this chapter.

2.1 SECOND-ORDER REACTION, FIRST-ORDER IN TWO COMPONENTS

As a model for a second-order process in two reactants, the reaction shown as

$$A + B \rightarrow \text{Products} \tag{2.1}$$

will be assumed to follow the rate law

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \tag{2.2}$$

Therefore, the reaction is first-order in both A and B and second-order overall. Such a reaction is referred to as a *second-order mixed case*, since the

concentrations of two reactants are involved. While the second-order case in one component was described in Chapter 1, the second-order mixed case is somewhat more complex. However, this type of rate law occurs very frequently because two-component reactions are very numerous. We can simplify the mathematical analysis in the following way. We will represent the initial concentration of A as $[A]_o$, and the concentration at some later time as [A]. The amount of A that has reacted after a certain time has elapsed is $[A]_o - [A]$. In Eq. (2.1), the balancing coefficients are assumed to be equal so that the amount of A reacting, $[A]_o - [A]$, must be equal to the amount of B reacting, $[B]_o - [B]$. Therefore, we can write

$$[A]_o - [A] = [B]_o - [B] \tag{2.3}$$

which can be solved for [B] to give

$$[B] = [B]_o - [A]_o + [A] \tag{2.4}$$

Substituting this expression for [B] in Eq. (2.2) yields

$$-\frac{d[A]}{dt} = k[A]([B]_o - [A]_o + [A]) \tag{2.5}$$

which can be rearranged to give

$$-\frac{d[A]}{[A]([B]_o - [A]_o + [A])} = k\ dt \tag{2.6}$$

Solving this equation requires using the technique known as the method of partial fractions. The fraction on the left hand side of Eq. (2.6) can be separated into two fractions by separating the denominator as follows.

$$\frac{1}{[A]([B]_o - [A]_o + [A])} = \frac{C_1}{[A]} + \frac{C_2}{[B]_o - [A]_o + [A]} \tag{2.7}$$

In this equation C_1 and C_2 are constants that must be determined. However, we know that the two fractions can be combined by using a single denominator, which can be shown as

$$\frac{C_1}{[A]} + \frac{C_2}{[B]_o - [A]_o + [A]} = \frac{C_1([B]_o - [A]_o + [A]) + C_2[A]}{[A]([B]_o - [A]_o + [A])} \tag{2.8}$$

Because the two sides of this equation are equal and because they are equal to the left hand side of Eq. (2.7), it should be clear that

$$C_1([B]_o - [A]_o + [A]) + C_2[A] = 1 \tag{2.9}$$

and that after performing the multiplication,

$$C_1[\mathrm{B}]_o - C_1[\mathrm{A}]_o + C_1[\mathrm{A}] + C_2[\mathrm{A}] = 1 \tag{2.10}$$

After an infinitely long time, we will assume that all of A has reacted so that [A] = 0 and

$$C_1[\mathrm{B}]_o - C_1[\mathrm{A}]_o = 1 = C_1\left([\mathrm{B}]_o - [\mathrm{A}]_o\right) \tag{2.11}$$

Therefore, by combining Eq. (2.11) with Eq. (2.10), it follows that after an infinite time of reaction,

$$C_1[\mathrm{B}]_o - C_1[\mathrm{A}]_o + C_1[\mathrm{A}] + C_2[\mathrm{A}] = 1 = C_1[\mathrm{B}]_o - C_1[\mathrm{A}]_o \tag{2.12}$$

This simplification is possible because

$$C_1[\mathrm{A}] + C_2[\mathrm{A}] = 0 \tag{2.13}$$

Because [A] can not be approximated as zero except after an infinite time, it follows that for Eq. (2.13) to be valid when [A] is not zero

$$C_1 + C_2 = 0 \tag{2.14}$$

which means that

$$C_1 = -C_2 \tag{2.15}$$

Therefore, from Eq. (2.11) we see that

$$1 = C_1\left([\mathrm{B}]_o - [\mathrm{A}]_o\right) \tag{2.16}$$

By making use of Eqs. (2.11) and 2.14), we find that

$$C_1 = \frac{1}{[\mathrm{B}]_o - [\mathrm{A}]_o} \text{ and } C_2 = -\frac{1}{[\mathrm{B}]_o - [\mathrm{A}]_o} \tag{2.17}$$

By substituting these values for C_1 and C_2, Eq. (2.6) can now be written as

$$-\frac{d[\mathrm{A}]}{([\mathrm{B}]_o - [\mathrm{A}]_o)[\mathrm{A}]} + \frac{d[\mathrm{A}]}{([\mathrm{B}]_o - [\mathrm{A}]_o)([\mathrm{B}]_o - [\mathrm{A}]_o + [\mathrm{A}])} = k\ dt \tag{2.18}$$

By grouping factors differently, this equation can also be written as

$$\frac{1}{([\mathrm{B}]_o - [\mathrm{A}]_o)}\left(-\frac{d[\mathrm{A}]}{[\mathrm{A}]}\right) + \left(\frac{1}{([\mathrm{B}]_o - [\mathrm{A}]_o)}\right)\frac{d[\mathrm{A}]}{([\mathrm{B}]_o - [\mathrm{A}]_o + [\mathrm{A}])} = k\ dt \tag{2.19}$$

Since $1/([B]_o - [A]_o)$ is a constant, integration of Eq. (2.19) yields

$$\frac{1}{[B]_o - [A]_o} \ln\left(\frac{[A]_o}{[A]}\right) + \left(\frac{1}{([B]_o - [A]_o)}\right) \ln\frac{([B]_o - [A]_o + [A])}{[B]_o} = kt \tag{2.20}$$

Combining terms on the left-hand side of Eq. (2.20), we obtain

$$\frac{1}{[B]_o - [A]_o} \ln\frac{[A]_o([B]_o - [A]_o + [A])}{[A][B]_o} = kt \tag{2.21}$$

However, from the stoichiometry of the reaction we know that

$$[B]_o - [A]_o + [A] = [B] \tag{2.22}$$

Therefore, by substituting this result in Eq. (2.21) we obtain

$$\frac{1}{[B]_o - [A]_o} \ln\frac{[A]_o[B]}{[A][B]_o} = kt \tag{2.23}$$

By making use of the relationship that $\ln(ab) = \ln a + \ln b$, we can write Eq. (2.23) as

$$\frac{1}{[B]_o - [A]_o} \ln\frac{[A]_o[B]}{[B]_o[A]} = \frac{1}{[B]_o - [A]_o}\left(\ln\frac{[A]_o}{[B]_o} + \ln\frac{[B]}{[A]}\right) = kt \tag{2.24}$$

This equation can be rearranged and simplified to yield

$$\frac{1}{[B]_o - [A]_o} \ln\frac{[A]_o}{[B]_o} + \frac{1}{[B]_o - [A]_o} \ln\frac{[B]}{[A]} = kt \tag{2.25}$$

which can also be written in the form

$$\ln\frac{[A]_o}{[B]_o} + \ln\frac{[B]}{[A]} = kt([B]_o - [A]_o) \tag{2.26}$$

Inspection of this equation shows that a plot of $\ln([B]/[A])$ versus t should be linear with a slope of $k([B]_o - [A]_o)$ and an intercept of $-\ln([A]_o/[B]_o)$. Consequently, Eq. (2.26) provides the basis for analyzing kinetic data for a mixed second-order reaction.

Frequently, an alternate way of describing a second-order process involving two reactants is employed in which the extent of reaction, x, is used as a variable. If the reaction is one in which the balancing coefficients

are both 1, the amounts of A and B reacted at any time will be equal. Therefore, we can write

$$\frac{dx}{dt} = k(a - x)(b - x) \tag{2.27}$$

where a and b are the initial concentrations of A and B, respectively, and x is the amount of each that has reacted. It follows that $(a - x)$ and $(b - x)$ are the concentrations of A and B *remaining* after the reaction is underway. Integration of this equation by the method of integration by parts yields

$$\frac{1}{b - a} \ln \frac{a(b - x)}{b(a - x)} = kt \tag{2.28}$$

which is analogous to Eq. (2.23). Another form of this equation is obtained by changing signs in the numerator and denominator, which gives

$$\frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)} = kt \tag{2.29}$$

This equation can also be written in the form

$$\ln \frac{(a - x)}{(b - x)} + \ln \frac{b}{a} = kt(a - b) \tag{2.30}$$

so that a graph of $\ln[(a - x)/(b - x)]$ versus t should be linear with a slope of $k(a - b)$ and an intercept of $-\ln(b/a)$.

A kinetic study of the hydrolysis of an ester can be used to illustrate the type of second-order process described in this section. For example, the hydrolysis of ethyl acetate produces ethyl alcohol and acetic acid.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH \tag{2.31}$$

When this reaction is carried out in basic solution, an excess of OH^- is added and part of it is consumed by reaction with the acetic acid that is produced.

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \tag{2.32}$$

Therefore, the extent of the reaction can be followed by titration of the unreacted OH^- when the amount of OH^- initially present is known. The number of moles of OH^- consumed will be equal to the number of moles of acetic acid produced. In the experiment described here, 125 ml of $CH_3COOC_2H_5$ solution at 30°C was mixed with 125 ml of NaOH solution at the same temperature so that the concentrations of reactants after mixing were 0.00582 **M** and 0.0100 **M**, respectively. If an aliquot is

removed from the reaction vessel and quenched by adding it to a solution containing an excess but known amount of HCl, the remaining OH^- will quickly be neutralized. By back-titrating the excess of HCl, one can determine the amount of HCl that is left unreacted, which makes it possible to determine how much OH^- has been consumed by the acetic acid generated by the reaction up to the time the aliquot was removed.

The data shown in Table 2.1 were obtained for the hydrolysis of 0.00582 **M** (the value of *b*) $CH_3COOC_2H_5$ at 30°C in 0.0100 **M** (the value of *a*) NaOH. The HCl used for quenching the reaction was 0.0203 **M**, and the titration of excess HCl was carried out using 0.0200 **M** NaOH. Aliquots were removed after certain reaction times, and each aliquot contained 25 ml of the reaction mixture.

When the data shown in Table 2.1 were used to prepare a second-order plot for the hydrolysis reaction as represented by Eq. (2.32), the result obtained was that shown in Figure 2.1. As expected, the plot is linear, and the slope can be determined graphically or by performing linear regression. In either case, the slope of the line represents the rate constant multiplied by $(a - b)$, which in this case is $(0.0100 - 0.0058) = 0.0042$. From linear regression, the slope was found to be 0.0356, so k is $0.0356/0.0042 = 8.47\,\mathbf{M}^{-1}\,\text{min}^{-1}$ or $0.141\,\mathbf{M}^{-1}\,\text{sec}^{-1}$.

The data shown in Table 2.1 were obtained for a reaction carried out at 30°C. Additional runs could be made at other temperatures to determine the rate constants, which could then be used to determine the activation energy for the reaction by means of the Arrhenius equation.

TABLE 2.1 Analysis of Kinetic Data for the Hydrolysis of Ethyl Acetate in NaOH Solution at 30°C.

Time, min	ml NaOH for back-titrating	Concentration of NaOH reacted	$\frac{(a-x)}{(b-x)}$	$\ln\frac{(a-x)}{(b-x)}$
1	13.83	0.00076	1.83	0.604
3	14.60	0.00112	1.90	0.642
5	15.40	0.00200	2.10	0.742
10	16.60	0.00300	2.50	0.916
20	17.95	0.00404	3.38	1.22
35	19.02	0.00488	5.57	1.72
55	19.68	0.00544	12.7	2.54
75	19.85	0.00558	25.3	3.23

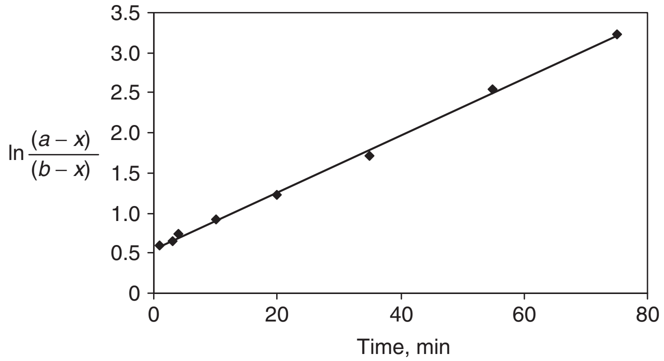


FIGURE 2.1 Second-order plot for the hydrolysis of ethyl acetate in basic solution.

2.2 THIRD-ORDER REACTIONS

In Sec. 2.1, we worked through the details of a second-order mixed reaction, which is first-order in each of two components. We will consider briefly here the various third-order cases (those involving reactants of multiple types are worked out in detail by Benson (1960)). The simplest case involves only one reactant for which the rate law can be written as

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^3 \tag{2.33}$$

Integration of this equation yields

$$\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}]_\mathrm{o}^2} = 2kt \tag{2.34}$$

Therefore, a plot of $1/[\mathrm{A}]^2$ versus time should be linear and have a slope of $2k$. After one half-life, $[\mathrm{A}] = [\mathrm{A}]_\mathrm{o}/2$ so substituting and simplifying gives

$$t_{1/2} = \frac{3}{2k[\mathrm{A}]_\mathrm{o}^2} \tag{2.35}$$

A third-order reaction can also arise from a reaction that can be shown in the form

$$a\mathrm{A} + b\mathrm{B} \rightarrow \text{ Products} \tag{2.36}$$

for which the observed rate law is

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2[\mathrm{B}] \tag{2.37}$$

However, the rate law could also involve $[\mathrm{A}][\mathrm{B}]^2$, but that case will not be described. If the stoichiometry is such that $[\mathrm{A}]_o - [\mathrm{A}] = [\mathrm{B}]_o - [\mathrm{B}]$, the integrated rate law is

$$\frac{1}{[\mathrm{B}]_o - [\mathrm{A}]_o}\left(\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_o}\right) + \frac{1}{([\mathrm{B}]_o - [\mathrm{A}]_o)^2}\ln\frac{[\mathrm{B}]_o[\mathrm{A}]}{[\mathrm{A}]_o[\mathrm{B}]} = kt \tag{2.38}$$

However, if the stoichiometry of the reaction is such that $[\mathrm{A}]_o - [\mathrm{A}] = 2([\mathrm{B}]_o - [\mathrm{B}])$, the integrated rate law can be shown to be

$$\frac{2}{2[\mathrm{B}]_o - [\mathrm{A}]_o}\left(\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_o}\right) + \frac{2}{(2[\mathrm{B}]_o - [\mathrm{A}]_o)^2}\ln\frac{[\mathrm{B}]_o[\mathrm{A}]}{[\mathrm{A}]_o[\mathrm{B}]} = kt \tag{2.39}$$

A reaction that involves three reactants can also be written in general form as

$$a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightarrow \text{Products} \tag{2.40}$$

We will assume that the stoichiometry of the reaction is such that equal numbers of moles of A, B, and C react. In that case, $[\mathrm{A}]_o - [\mathrm{A}] = [\mathrm{B}]_o - [\mathrm{B}] = [\mathrm{C}]_o - [\mathrm{C}]$ and the third-order rate law has the form

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}][\mathrm{C}] \tag{2.41}$$

Obtaining the integrated form of this third-order mixed rate law involving three reactants presents a difficult problem. However, after making the substitutions for [B] and [C] by noting that they can be replaced by $[\mathrm{B}] = [\mathrm{B}]_o - [\mathrm{A}]_o + [\mathrm{A}]$ and $[\mathrm{C}] = [\mathrm{C}]_o - [\mathrm{A}]_o + [\mathrm{A}]$, some very laborious mathematics yields the rate law in integrated form as

$$\frac{1}{\mathrm{LMN}}\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_o}\right)^{\mathrm{M}}\left(\frac{[\mathrm{B}]}{[\mathrm{B}]_o}\right)^{\mathrm{N}}\left(\frac{[\mathrm{C}]}{[\mathrm{C}]_o}\right)^{\mathrm{L}} = kt \tag{2.42}$$

where $\mathrm{L} = [\mathrm{A}]_o - [\mathrm{B}]_o$, $\mathrm{M} = [\mathrm{B}]_o - [\mathrm{C}]_o$, and $\mathrm{N} = [\mathrm{C}]_o - [\mathrm{A}]_o$. In addition to the cases involving two or three components just described, there are other systems that could be considered. However, it is not necessary to work through the mathematics of all of these cases. It is sufficient to show that all such cases have been described mathematically.

2.3 PARALLEL REACTIONS

In addition to the reaction schemes described earlier, there are many other types of systems that are quite common. In one of these, a single reactant may be converted into several different products simultaneously. There are numerous examples of such reactions in organic chemistry. For example, the reaction of toluene with bromine in the presence of iron at 25°C produces 65% *p*–bromotoluene and 35% *o*–bromotoluene. Similarly, the nitration of toluene under different conditions can lead to different amounts of *o*–nitrotoluene and *p*–nitrotoluene, but a mixture of these products is obtained in any event. Tailoring the conditions of a reaction to obtain the most favorable distribution of products is a common practice in synthetic chemistry. We will now illustrate the mathematical analysis of the kinetics of such reactions.

Suppose a compound, A, undergoes reactions to form several products, B, C, and D, at different rates. We can show this system as

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{2.43}$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{C} \tag{2.44}$$

$$\mathrm{A} \xrightarrow{k_3} \mathrm{D} \tag{2.45}$$

The rate of disappearance of A is the sum of the rates for the three processes, so we can write

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] + k_2[\mathrm{A}] + k_3[\mathrm{A}] = (k_1 + k_2 + k_3)[\mathrm{A}] \tag{2.46}$$

Prior to integration, this equation can be written as

$$-\int_{[\mathrm{A}]_o}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = (k_1 + k_2 + k_3)\int_0^t dt \tag{2.47}$$

The sum of three rate constants is simply a constant, so integration is analogous to that of the first-order case and yields

$$\ln\frac{[\mathrm{A}]_o}{[\mathrm{A}]} = (k_1 + k_2 + k_3)t \tag{2.48}$$

Equation (2.48) can also be written in exponential form as

$$[\mathrm{A}] = [\mathrm{A}]_o e^{-(k_1+k_2+k_3)t} \tag{2.49}$$

The product B is produced only in the first of the three reactions, so the rate of formation can be written as

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_o e^{-(k_1+k_2+k_3)t} \tag{2.50}$$

Letting $k = k_1 + k_2 + k_3$, rearrangement yields

$$d[\mathrm{B}] = k_1[\mathrm{A}]_o e^{-kt} dt \tag{2.51}$$

Therefore, obtaining the expression for [B] involves integrating the equation

$$\int_{[\mathrm{B}]_o}^{[\mathrm{B}]} d[\mathrm{B}] = k_1[\mathrm{A}]_o \int_0^t e^{-kt} dt \tag{2.52}$$

Integration of Eq. (2.52) leads to

$$[\mathrm{B}] = [\mathrm{B}]_o + \frac{k_1[\mathrm{A}]_o}{k}(1 - e^{-kt}) \tag{2.53}$$

and substituting for k gives

$$[\mathrm{B}] = [\mathrm{B}]_o + \frac{k_1[\mathrm{A}]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t}) \tag{2.54}$$

If no B is present at the beginning of the reaction, $[\mathrm{B}]_o = 0$ and the equation simplifies to

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t}) \tag{2.55}$$

In a similar way, the expressions can be obtained that give [C] and [D] as functions of time. These can be written as

$$[\mathrm{C}] = [\mathrm{C}]_o + \frac{k_2[\mathrm{A}]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t}) \tag{2.56}$$

$$[\mathrm{D}] = [\mathrm{D}]_o + \frac{k_3[\mathrm{A}]_o}{k_1 + k_2 + k_3}(1 - e^{-(k_1+k_2+k_3)t}) \tag{2.57}$$

If, as is the usual case, no B, C, or D is initially present, $[\mathrm{B}]_o = [\mathrm{C}]_o = [\mathrm{D}]_o = 0$, and the ratio of Eqs. (2.55) and (2.56) gives

$$\frac{[\mathrm{B}]}{[C]} = \frac{\dfrac{k_1[\mathrm{A}]_o}{k_1 + k_2 + k_3}}{\dfrac{k_2[\mathrm{A}]_o}{k_1 + k_2 + k_3}} \frac{(1 - e^{-(k_1+k_2+k_3)t})}{(1 - e^{-(k_1+k_2+k_3)t})} = \frac{k_1}{k_2} \tag{2.58}$$

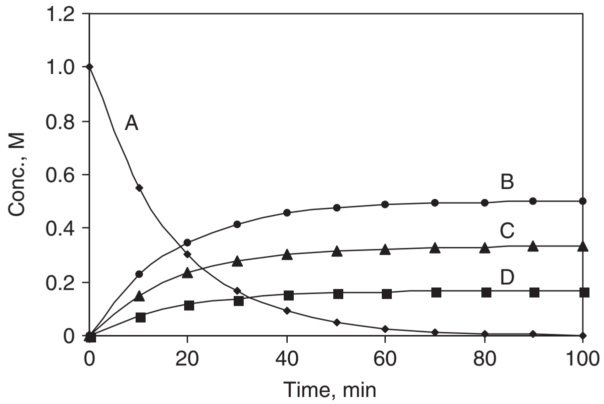


FIGURE 2.2 Concentration of reactant and products for parallel first-order reactions.

Similarly, it can be shown that

$$\frac{[B]}{[D]} = \frac{k_1}{k_3} \tag{2.59}$$

In order to illustrate the relationships between concentrations graphically, the case where $[A]_o = 1.00\,\mathbf{M}$ and $k_1 = 0.03$, $k_2 = 0.02$, and $k_3 = 0.01\ \text{min}^{-1}$ was used in the calculations. The resulting graph is shown in Figure 2.2. In this diagram, the sum of [A] + [B] + [C] + [D] is equal to 1.00 **M**. For all time values, the ratios of concentrations [B]:[C]:[D] is the same as k_1: k_2: k_3.

2.4 SERIES FIRST-ORDER REACTIONS

It is by no means an uncommon situation for a chemical reaction to take place in a series of steps such as

$$\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C} \tag{2.60}$$

Such a sequence is known as *series* or *consecutive* reactions. In this case, B is known as an *intermediate* because it is not the final product. A similar situation is very common in nuclear chemistry where a nuclide decays to a daughter nuclide that is also radioactive and undergoes decay (see Chapter 9). For simplicity, only the case of first-order reactions will be discussed.

The rate of disappearance of A can be written as

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] \tag{2.61}$$

The net change in the concentration of B is the rate at which it is formed minus the rate at which it reacts. Therefore,

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{2.62}$$

where the term $k_1[\mathrm{A}]$ represents the formation of B from A, and the term $-k_2[\mathrm{B}]$ represents the reaction of B to form C. The rate of formation of C can be represented as

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \tag{2.63}$$

If the stoichiometry as shown in Eq. (2.60) is followed, it should be apparent that

$$[\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}] = [\mathrm{A}]_o \tag{2.64}$$

Equation (2.61) represents a first-order process, so it can be integrated to yield

$$[\mathrm{A}] = [\mathrm{A}]_o e^{-k_1 t} \tag{2.65}$$

Substituting this expression for [A] in Eq. (2.62) gives

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_o e^{-k_1 t} - k_2[\mathrm{B}] \tag{2.66}$$

Rearrangement of this equation leads to

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] - k_1[\mathrm{A}]_o e^{-k_1 t} = 0 \tag{2.67}$$

An equation of this type is known as a linear differential equation with constant coefficients. We will now demonstrate the solution of an equation of this type. If we assume a solution of the form

$$[\mathrm{B}] = u e^{-k_2 t} \tag{2.68}$$

then by differentiation we obtain

$$\frac{d[\mathrm{B}]}{dt} = -u k_2 e^{-k_2 t} + e^{-k_2 t}\frac{du}{dt} \tag{2.69}$$

Substituting the right-hand side of this equation for $d[\mathrm{B}]/dt$ in Eq. (2.67), we obtain

$$-uk_2\mathrm{e}^{-k_2t} + \mathrm{e}^{-k_2t}\frac{du}{dt} = k_1[\mathrm{A}]_\mathrm{o}\mathrm{e}^{-k_1t} - uk_2e^{-k_2t} \tag{2.70}$$

which can be simplified to yield

$$\mathrm{e}^{-k_2t}\frac{du}{dt} = k_1[\mathrm{A}]_\mathrm{o}e^{-k_1t} \tag{2.71}$$

Dividing both sides of this equation by $\exp(-k_2t)$ gives

$$\frac{du}{dt} = k_1[\mathrm{A}]_\mathrm{o}\mathrm{e}^{-(k_1-k_2)t} \tag{2.72}$$

Integration of this equation yields

$$u = \frac{k_1}{k_2 - k_1}[\mathrm{A}]_\mathrm{o}\mathrm{e}^{-(k_1-k_2)t} + C \tag{2.73}$$

where C is a constant. Having assumed that the solution has the form

$$[\mathrm{B}] = u\mathrm{e}^{-k_2t} \tag{2.74}$$

we can combine Eqs. (2.73) and (2.74) to obtain

$$[\mathrm{B}] = u\mathrm{e}^{-k_2t} = \frac{k_1[\mathrm{A}]_\mathrm{o}}{k_2 - k_1}\mathrm{e}^{-k_1t} + C\mathrm{e}^{-k_2t} \tag{2.75}$$

If we let $[\mathrm{B}]_\mathrm{o}$ be the concentration of B that is present at $t = 0$, Eq. (2.75) reduces to

$$[\mathrm{B}]_\mathrm{o} = \frac{k_1[\mathrm{A}]_\mathrm{o}}{k_2 - k_1} + C \tag{2.76}$$

Solving for C and substituting the resulting expression in Eq. (2.75) yields

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_\mathrm{o}}{k_2 - k_1}(\mathrm{e}^{-k_1t} - \mathrm{e}^{-k_2t}) + [\mathrm{B}]_\mathrm{o}\mathrm{e}^{-k_2t} \tag{2.77}$$

The first term on the right-hand side of Eq. (2.77) represents the reaction of B that is produced by the disappearance of A, while the second term describes the reaction of any B that is initially present. If, as is the usual case, $[\mathrm{B}]_\mathrm{o} = 0$, Eq. (2.77) reduces to

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_\mathrm{o}}{k_2 - k_1}(\mathrm{e}^{-k_1t} - \mathrm{e}^{-k_2t}) \tag{2.78}$$

If this result and that shown for [A] in Eq. (2.65) are substituted into Eq. (2.64), solving for [C] gives

$$[C] = [A]_o\left(1 - \frac{1}{k_2 - k_1}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right) \tag{2.79}$$

A number of interesting cases can arise depending on the relative magnitudes of k_1 and k_2. Figure 2.3 shows the unlikely case where $k_1 = 2k_2$. Such a case involving a large concentration of the intermediate is unlikely because the intermediate, B, is usually *more* reactive than the starting compound. This situation is illustrated in Figure 2.4, which was generated assuming that $k_2 = 2k_1$. In this case, it is apparent that there is a less rapid decrease in [A] and a slower buildup of B in the system. Because of the particular relationships chosen for the rate constants in the two examples ($k_1 = 2k_2$ and $k_2 = 2k_1$), the rate of production of C is unchanged in the two cases.

Figure 2.5 shows the case where $k_2 = 10k_1$ as a realistic example of a system in which the intermediate is very reactive. In this case, the concentration of B is always low, which is a more likely situation for an intermediate. Also, the concentration of C always shows an acceleratory nature in the early portion of the reaction. Further, over a large extent of reaction, the concentration of B remains essentially constant. Note that in all three cases, the curve representing the concentration of C is sigmoidal in shape as C is produced at an accelerating rate as the intermediate reacts.

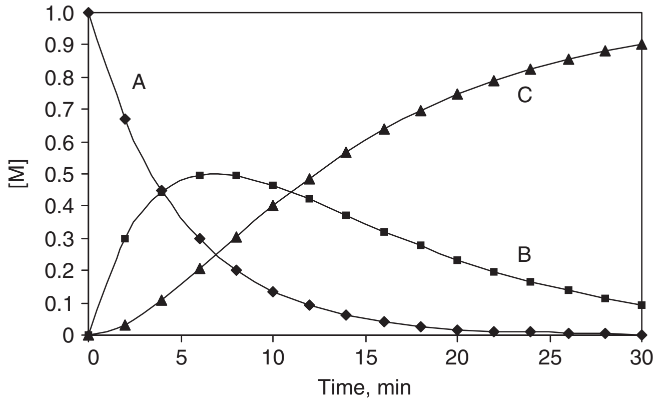


FIGURE 2.3 Series first-order reactions where $[A]_o = 1.00\,\mathbf{M}$, $k_1 = 0.200\ \text{min}^{-1}$, and $k_2 = 0.100\,\text{min}^{-1}$.

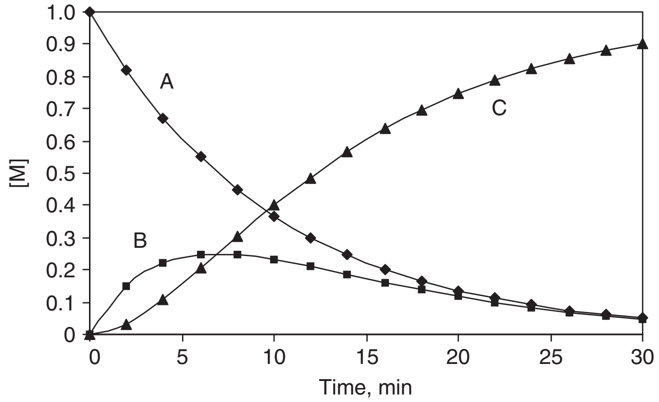


FIGURE 2.4 Series first-order reactions where $[A]_o = 1.00\,\mathbf{M}$, $k_1 = 0.100\ \text{min}^{-1}$, and $k_2 = 0.200\,\text{min}^{-1}$.

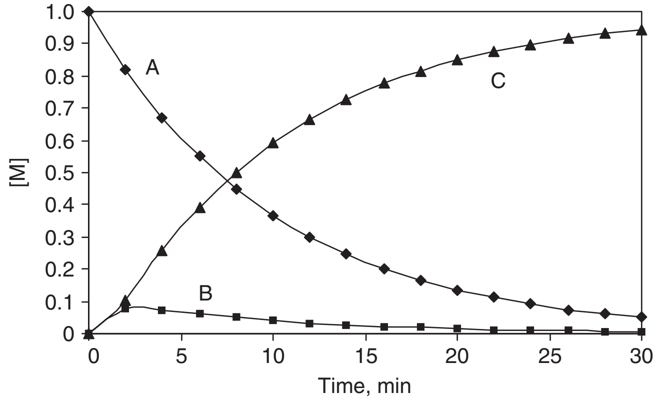


FIGURE 2.5 Series first-order reactions where $[A]_o = 1.00\,\mathbf{M}$, $k_1 = 0.100\ \text{min}^{-1}$, and $k_2 = 1.00\,\text{min}^{-1}$.

Therefore, we conclude that when $k_2 > k_1$, there is a low and essentially constant concentration of the intermediate. Because of this, $d[B]/dt$ is approximately 0, which can be shown as follows. For this system of first-order reactions,

$$[A] + [B] + [C] = [A]_o \tag{2.80}$$

which, because [B] is nearly 0 can be approximated by

$$[A] + [C] = [A]_o \tag{2.81}$$

Taking the derivatives with respect to time, we obtain

$$\frac{d[\mathrm{A}]}{dt}+\frac{d[\mathrm{B}]}{dt}+\frac{d[\mathrm{C}]}{dt}=0 \tag{2.82}$$

and

$$\frac{d[\mathrm{A}]}{dt}+\frac{d[\mathrm{C}]}{dt}=0 \tag{2.83}$$

Therefore, $d[\mathrm{B}]/dt=0$ and [B] remains essentially constant throughout most of the reaction. For the case where $k_2 = 10k_1$, and $[\mathrm{A}]_o = 1.00\,\mathbf{M}$ (shown in Figure 2.5), [B] never rises above 0.076 **M**, and it varies only from 0.076 **M** to 0.033 **M** in the time interval from $t=2$ min to $t=12$ min during which time [A] varies from 0.819 **M** to 0.301 **M** and [C] varies from 0.105 **M** to 0.666 **M**. The approximation made by considering the concentration of the intermediate to be essentially constant is called the *steady-state* or *stationary state approximation.*

It should be clear from Figures 2.3 through 2.5 that [B] goes through a maximum, which is to be expected. The time necessary to reach that maximum concentration of B, which we identify as t_m, can easily be calculated. At that time, $d[\mathrm{B}]/dt=0$. If Eq. (2.78) is differentiated with respect to time and the derivative is set equal to zero, we obtain

$$\frac{d[\mathrm{B}]}{dt}=\frac{-k_1k_1[\mathrm{A}]_o}{k_2-k_1}\mathrm{e}^{-k_1t}+\frac{k_1k_2[\mathrm{A}]_o}{k_2-k_1}\mathrm{e}^{-k_2t}=0 \tag{2.84}$$

Therefore,

$$\frac{k_1k_1[\mathrm{A}]_o}{k_2-k_1}\mathrm{e}^{-k_1t}=\frac{k_1k_2[\mathrm{A}]_o}{k_2-k_1}\mathrm{e}^{-k_2t} \tag{2.85}$$

Canceling like terms from both sides of the equation gives

$$k_1\mathrm{e}^{-k_1t}=k_2\mathrm{e}^{-k_2t} \tag{2.86}$$

which can also be written as

$$\frac{k_1}{k_2}=\frac{\mathrm{e}^{-k_2t}}{\mathrm{e}^{-k_1t}}=\mathrm{e}^{-k_2t}e^{k_1t}=\mathrm{e}^{(k_1-k_2)t} \tag{2.87}$$

Taking the logarithm of both sides of this equation gives

$$\ln\left(\frac{k_1}{k_2}\right)=(k_1-k_2)t \tag{2.88}$$

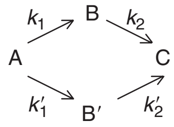
which yields the time necessary to reach the maximum in the curve representing [B] as a function of time. Representing that time as t_m and solving for that quantity, we obtain

$$t_m = \frac{\ln \dfrac{k_1}{k_2}}{k_1 - k_2} \tag{2.89}$$

The concentration of the intermediate after different reaction times is usually determined by removing a sample from the reaction mixture, quenching it by an appropriate means, and analyzing quantitatively for B. If k_1 has been measured by following the disappearance of A and the concentration of B has been determined sufficiently that t_m can be determined experimentally, it is possible to use Eq. (2.89) to determine k_2, the rate constant for the reaction of the intermediate. However, solving Eq. (2.89) for k_2 when numerical values are available for t_m and k_1 requires a graphical or iterative technique. Such procedures are easily carried out using a graphing calculator.

2.5 SERIES REACTIONS WITH TWO INTERMEDIATES

Although we have just presented the analysis of a system in which one intermediate is formed during the reaction, there are also cases in which two intermediates are formed, both of which subsequently react to form product. This scheme can be shown as



(2.90)

The disappearance of A is the result of two reactions that represent a series of first-order reactions that have rate constants k_1 and k_1'. Therefore, the rate law can be written as

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_1')[\mathrm{A}] \tag{2.91}$$

The solution of a rate equation of this type has already been shown, and the result is

$$[\mathrm{A}] = [\mathrm{A}]_o e^{-(k_1+k_1')t} \tag{2.92}$$

The intermediate B is produced by a reaction that has a rate given by $k_1[A]$, and it is consumed in a reaction that has a rate of $k_2[B]$. Therefore, the equation for the change in [B] with time can be shown as

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \tag{2.93}$$

In an analogous way, the rate law for the reactions involving intermediate B′ is

$$\frac{d[B']}{dt} = k_1'[A] - k_2'[B'] \tag{2.94}$$

The product, C, is produced by the reaction of the two intermediates, so the rate law can be written as

$$\frac{d[C]}{dt} = k_2[B] + k_2'[B'] \tag{2.95}$$

After substituting for [A] the expression shown in Eq. (2.92) and rearranging, we can write Eqs. (2.93) and (2.94) as follows.

$$\frac{d[B]}{dt} + k_2[B] - k_1[A]_o e^{-(k_1+k_1')t} = 0 \tag{2.96}$$

$$\frac{d[B']}{dt} + k_2'[B'] - k_1'[A]_o e^{-(k_1+k_1')t} = 0 \tag{2.97}$$

Although details of the solution will not be shown, these equations are linear differential equations that can be solved by standard techniques to give

$$[B] = \frac{k_1[A]_o}{k_2 - k_1}(e^{-(k_1+k_1')t} - e^{-k_2 t}) \tag{2.98}$$

$$[B'] = \frac{k_1'[A]_o}{k_2' - k_1'}(e^{-(k_1+k_1')t} - e^{-k_2' t}) \tag{2.99}$$

Figure 2.6 shows how the concentrations of the two intermediates will vary with time for a specific case for which $[A]_o = 1.00\,\mathbf{M}$, and the rate constants are assumed to be $k_1 = 0.050$, $k_2 = 0.150$, $k_1' = 0.040$, and $k_2' = 0.120$ all in min^{-1}. Note that the two intermediates will not be present in maximum concentrations at exactly the same time unless $k_1 = k_1'$, which is very unlikely.

Since both B and B′ are produced by the reaction of A, the most rapid rate of their production is at the beginning of the reaction, and the rate is deceleratory thereafter.

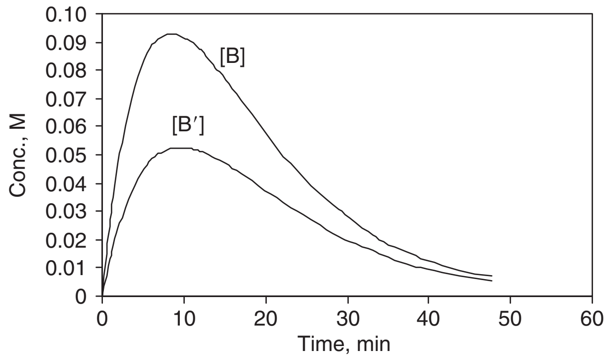


FIGURE 2.6 Concentration of intermediates B and B′ in the reaction scheme shown in Eq. (2.90) using rate constants given in the text.

If only A is present at the beginning of the reaction, the material balance requires that at any later time

$$[A] + [B] + [B'] + [C] = [A]_o \tag{2.100}$$

so that the concentration of C can be described as

$$[C] = [A]_o - [B] - [B'] - [A] \tag{2.101}$$

Expressions for all of the quantities on the right-hand side of Eq. (2.101) have already been found, so by substitution we obtain

$$\begin{aligned}[C] = [A]_o &- \frac{k_1[A]_o}{k_2 - k_1}(e^{-(k_1+k_1')t} - e^{-k_2 t}) \\ &- \frac{k_1'[A]_o}{k_2' - k_1'}(e^{-(k_1+k_1')t} - e^{-k_2' t}) - [A]_o\, e^{-(k_1+k_1')t}\end{aligned} \tag{2.102}$$

By factoring $[A]_o$ out of each term on the right-hand side of this equation, it can be written as

$$\begin{aligned}[C] = [A]_o \Bigg[1 &- \frac{k_1}{k_2 - k_1}(e^{-(k_1+k_1')t} - e^{-k_2 t}) \\ &- \frac{k_1'}{k_2' - k_1'}(e^{-(k_1+k_1')t} - e^{-k_2' t}) - e^{-(k_1+k_1')t}\Bigg]\end{aligned} \tag{2.103}$$

The time necessary to reach the maximum concentrations of the intermediates can be found in a way that is analogous to that illustrated in the previous section. Differentiating Eqs. (2.98) and (2.99) with respect to time and setting the derivatives equal to zero, we find that the time to reach the maximum concentration of B is given by

$$t_m = \frac{\ln\left(\dfrac{k_1 + k_1'}{k_2}\right)}{k_1 + k_1' - k_2} \tag{2.104}$$

while the time necessary to reach the maximum concentration of B′ is

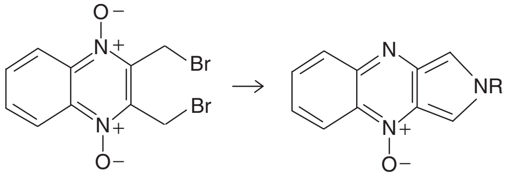
$$t_m' = \frac{\ln\left(\dfrac{k_1 + k_1'}{k_2'}\right)}{k_1 + k_1' - k_2'} \tag{2.105}$$

Because the sum $k_1 + k_1'$ is easily obtained by determining the rate of disappearance of A, measuring the time to maximum concentrations of B and B′ enables k_2 and k_2', respectively, to be determined. However, the resulting equations must be solved numerically. It should also be noted that after passing the maxima in the concentrations of the intermediates, the decrease in their concentrations can be approximated fairly well by a first-order rate law. It is possible to extend the system to include three intermediates, but the derivations are laborious and of more limited usefulness.

Another reaction scheme that involves two intermediates can be described by the equation

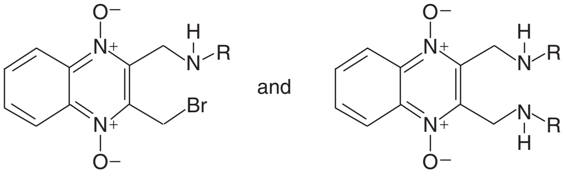
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \tag{2.106}$$

In this process, the intermediates are formed sequentially rather than simultaneously as in the previously discussed case. This reaction scheme has recently been shown by Pearson, et al. (2005) to be consistent with the kinetic data obtained for the reaction (which takes place in several steps)



(2.107)

When carried out so that R = $n-C_4H_9$, this reaction appears to involve primarily the two intermediates



although other intermediates were found in minor amounts. The four compounds shown in the equation and as intermediates accounted for >90% of the material present.

The kinetic analysis of this system is based on the following equations.

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] \tag{2.108}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{2.109}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] - k_3[\mathrm{C}] \tag{2.110}$$

$$\frac{d[\mathrm{D}]}{dt} = k_3[\mathrm{C}] \tag{2.111}$$

In fact, the equations relating the concentrations of A and B with time are exactly the same as in the model for a single intermediate. The fact that C undergoes subsequent reaction has no effect on the concentrations of A and B. Although the details will not be presented, the solution of these equations is analogous to that used in the case of one intermediate. The results are as follows.

$$[\mathrm{A}] = [\mathrm{A}]_o e^{-k_1 t} \tag{2.112}$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_o}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{2.113}$$

$$[\mathrm{C}] = k_1 k_2 [\mathrm{A}]_o \left(\frac{e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_1)} - \frac{e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_3 - k_1)(k_3 - k_2)} \right) \tag{2.114}$$

$$[\mathrm{D}] = [\mathrm{A}]_o \left(1 - \frac{k_2 k_3 e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{k_1 k_3 e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_2)} - \frac{k_1 k_2 e^{-k_3 t}}{(k_3 - k_1)(k_3 - k_2)} \right) \tag{2.115}$$

The relationship between the various species can be illustrated by considering a model in which the initial concentration of A is assumed to be 1.00 **M** and the other species are assumed to be absent at the beginning of the reaction. For illustration, we will let $k_1 = 0.200$, $k_2 = 0.100$, and $k_3 = 0.150\ \mathrm{min}^{-1}$. The results are shown in Figure 2.7. Note the acceleratory nature of the curve representing the concentration of C in the early stages of the reaction.

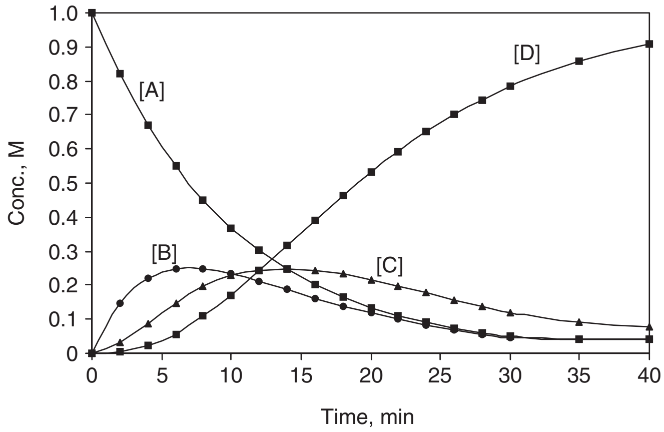


FIGURE 2.7 Concentrations of species in the reaction shown in Eq. (2.106) with conditions described in the text.

The curves presented by Pearson, et al. for the concentrations of the reactant and product shown in Eq. (2.107) and for the intermediates exhibit the same general shape as do those shown in Figure 2.7.

It is interesting to note that the schemes shown in Eqs. (2.90) and 2.(106) result in concentration versus time curves that have the same *general* features. Whether the intermediates grow sequentially or simultaneously, the concentration of each intermediate passes through a maximum and then decreases exponentially. However, in the case of sequential intermediates, the curve showing the concentration of C with time shows an acceleratory period as it is produced at an increasing rate as B reacts. In the case of simultaneous intermediates, the maximum rate of their production is the initial rate when the concentration of A is highest because both are formed as A reacts. However, depending on the rates at which the intermediates are produced and react, it may be difficult to distinguish the acceleratory nature of the curve representing the concentration of C. Without knowing the relative rates of formation of the intermediates, there would be no way *a priori* to identify which reaction scheme is applicable in a given case. Certainly there are many reactions that follow one of these mechanisms involving two intermediates.

2.6 REVERSIBLE REACTIONS

Many reactions do not proceed to completion, and the extent of reversibility must be considered even from the early stages of the reaction.

To illustrate the kinetic analysis, a first-order reaction will be considered, which is the simplest case.

Consider the reaction

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{2.116}$$

Because A is disappearing in the forward reaction and is produced by the reverse reaction, it should be clear that

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{2.117}$$

Assuming that only A is initially present, the concentration of B is expressed as

$$[\mathrm{B}] = [\mathrm{A}]_o - [\mathrm{A}] \tag{2.118}$$

Substituting for [B] in Eq. (2.117) gives

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}([\mathrm{A}]_o - [\mathrm{A}]) \tag{2.119}$$

Therefore,

$$-d[\mathrm{A}] = \{k_1[\mathrm{A}] - k_{-1}([\mathrm{A}]_o - [\mathrm{A}])\}dt \tag{2.120}$$

which can be written as

$$-\frac{d[\mathrm{A}]}{(k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_o} = dt \tag{2.121}$$

This equation must be integrated between the limits of $[\mathrm{A}]_o$ at $t = 0$ and [A] at a later time t so the integral equation is

$$-\int_{[\mathrm{A}]_o}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{(k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_o} = \int_0^t dt \tag{2.122}$$

The integral on the left-hand side of Eq. (2.122) is a common form that can readily be found in a table of integrals. The integration can be represented as

$$\int \frac{dx}{a + bx} = \frac{1}{b}\ln(a + bx) \tag{2.123}$$

In this case, $b = (k_1 + k_{-1})$ and $a = -k_{-1}[\mathrm{A}]_o$. Therefore,

$$-\frac{1}{k_1 + k_{-1}} \ln\{(k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_o\}\Big|_{[\mathrm{A}]_o}^{[\mathrm{A}]} = t \tag{2.124}$$

which must be evaluated between the lower limit of $[\mathrm{A}]_o$ at time zero and an upper limit of [A] at time t. Multiplying both sides of Eq. (2.124) by $(k_1 + k_{-1})$ and expanding the left-hand side by making use of the limits, we obtain

$$-[\ln\{(k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_o\} - \ln\{(k_1 + k_{-1})[\mathrm{A}]_o - k_{-1}[\mathrm{A}]_o\}] = (k_1 + k_{-1})t \tag{2.125}$$

which can be simplified to give the integrated rate equation

$$\ln\frac{k_1[\mathrm{A}]_o}{(k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_o} = (k_1 + k_{-1})t \tag{2.126}$$

However, the equation needed for purposes of analyzing kinetic data should be in a form that involves the concentration of A when equilibrium is reached. Such an equation can be obtained in the following way.

As equilibrium is approached at infinite time, $t \rightarrow t_f$ and $d[\mathrm{A}]/dt = 0$.

$$\frac{d[\mathrm{A}]}{dt} = 0 = k_1[\mathrm{A}]_f - k_{-1}[\mathrm{B}]_f \tag{2.127}$$

Therefore, when equilibrium has been reached

$$k_1[\mathrm{A}]_f = k_{-1}[\mathrm{B}]_f = k_{-1}([\mathrm{A}]_o - [\mathrm{A}]_f) = k_{-1}[\mathrm{A}]_o - k_{-1}[\mathrm{A}]_f \tag{2.128}$$

where $[\mathrm{A}]_f$ is the equilibrium concentration of A. Solving for the concentration of A at infinite time gives

$$[\mathrm{A}]_f = \frac{k_{-1}[\mathrm{A}]_o}{k_1 + k_{-1}} \tag{2.129}$$

which allows us to write $[\mathrm{A}]_o$ as

$$[\mathrm{A}]_o = \frac{(k_1 + k_{-1})[\mathrm{A}]_f}{k_{-1}} \tag{2.130}$$

Substituting this value for $[\mathrm{A}]_o$ in Eq. (2.126), we obtain

$$\ln\frac{\dfrac{k_1(k_1 + k_{-1})[\mathrm{A}]_f}{k_{-1}}}{(k_1 + k_{-1})[\mathrm{A}] - k_{-1}\left(\dfrac{(k_1 + k_{-1})[\mathrm{A}]_f}{k_{-1}}\right)} = (k_1 + k_{-1})t \tag{2.131}$$

Simplifying the denominator on the left-hand side of this equation yields

$$\ln \frac{\dfrac{k_1(k_1 + k_{-1})[\mathrm{A}]_\mathrm{f}}{k_{-1}}}{(k_1 + k_{-1})([\mathrm{A}] - [\mathrm{A}]_\mathrm{f})} = (k_1 + k_{-1})t \tag{2.132}$$

Because $[\mathrm{B}]_\mathrm{f} = [\mathrm{A}]_\mathrm{o} - [\mathrm{A}]_\mathrm{f}$, we can write $k_1[\mathrm{A}] = k_{-1}([\mathrm{A}]_\mathrm{o} - [\mathrm{A}]_\mathrm{f})$. Substituting for $k_1[\mathrm{A}]_\mathrm{f}$ in the numerator gives

$$\ln \frac{k_{-1}([\mathrm{A}]_\mathrm{o} - [\mathrm{A}]_\mathrm{f})\dfrac{k_1 + k_{-1}}{k_{-1}}}{(k_1 + k_{-1})([\mathrm{A}] - [\mathrm{A}]_\mathrm{f})} = \ln \frac{(k_1 + k_{-1})([\mathrm{A}]_\mathrm{o} - [\mathrm{A}]_\mathrm{f})}{(k_1 + k_{-1})([\mathrm{A}] - [\mathrm{A}]_\mathrm{f})} = (k_1 + k_{-1})t \tag{2.133}$$

Simplifying this equation gives the equation for the infinite time or equilibrium condition, which can be written as

$$\ln \frac{[\mathrm{A}]_\mathrm{o} - [\mathrm{A}]_\mathrm{f}}{[\mathrm{A}] - [\mathrm{A}]_\mathrm{f}} = (k_1 + k_{-1})t \tag{2.134}$$

which can be written in exponential form as

$$[\mathrm{A}] = [\mathrm{A}]_\mathrm{f} + ([\mathrm{A}]_\mathrm{o} - [\mathrm{A}]_\mathrm{f})e^{-(k_1+k_{-1})t} \tag{2.135}$$

From Eq. (2.134), we see that for this reversible first-order system a plot of $\ln([\mathrm{A}] - [\mathrm{A}]_\mathrm{f})$ versus time should be linear and have a slope of $-(k_1 + k_{-1})$.

We will illustrate these ideas by considering a hypothetical reaction for which $[\mathrm{A}]_\mathrm{o} = 1.000\,\mathbf{M}$, $k_1 = 0.050\ \mathrm{min}^{-1}$, and $k_{-1} = 0.010\ \mathrm{min}^{-1}$ and for which the equilibrium constant has a value of 5.00. Then, for the reaction

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{2.136}$$

$$\mathrm{K} = \frac{[\mathrm{B}]_\mathrm{f}}{[\mathrm{A}]_\mathrm{f}} = 5.00 = \frac{x}{1.00 - x} \tag{2.137}$$

where x is the amount of both A and B that have reacted. Solving for x we find that $x = 0.167$ **M**, which is the equilibrium concentration of A. By using the parameters given, we can calculate the concentration of A as a function of time, and the results obtained are shown in Table 2.2.

The data shown in Table 2.2 were used to prepare the plot of $\ln([\mathrm{A}] - [\mathrm{A}]_\mathrm{f})$ versus time that is shown in Figure 2.8. In accord with Eq. (2.124) this linear plot has a slope that is precisely $-(k_1 + k_{-1})$.

If the reaction is very slow, it is difficult to determine $[\mathrm{A}]_\mathrm{f}$ accurately, and, therefore, the limiting accuracy $[\mathrm{A}]_\mathrm{f} \pm \Delta[\mathrm{A}]_\mathrm{f}$ is actually known where

TABLE 2.2 Data for the Reversible Reaction Described in the Text.

Time, min	[A], **M**
0	1.00
5	0.784
10	0.624
15	0.505
20	0.418
30	0.304
40	0.242
50	0.208
60	0.189
70	0.179
80	0.174

Δ is the experimental error in the concentration of A. Using the arbitrary error of 0.033 **M** in $[A]_f$ with the case described previously, $[A]_f$ could vary from 0.133 to 0.200 **M**. When these errors are introduced and Eq. (2.125) is used to calculate [A] as a function of time, the results obtained are those shown in Figure 2.9.

For many reversible reactions, it is not possible to study the later stages of the reaction, so the early part of the reaction is used to provide data for analysis. For example, it is instructive to consider the *initial* rate of the reaction A $\rightarrow$ B

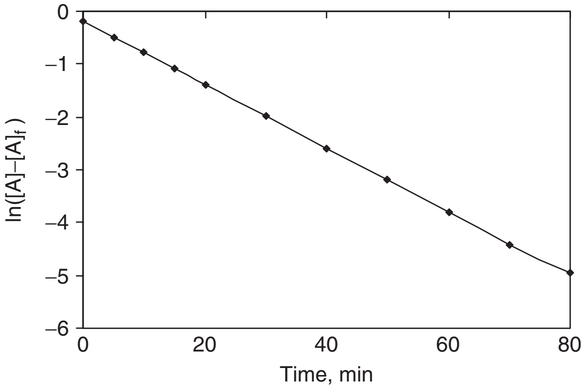


FIGURE 2.8 A plot for a reversible reaction constructed using the conditions described in the text.

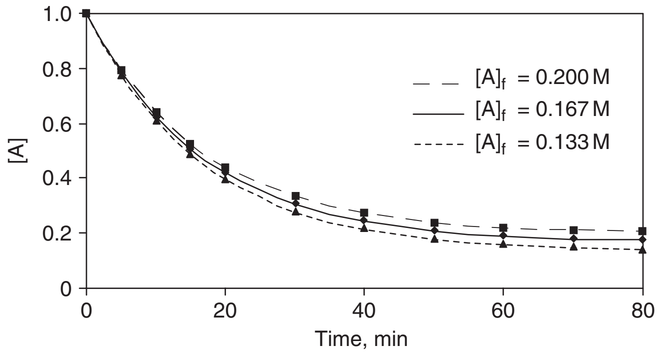


FIGURE 2.9 Variation in [A] when $[A]_f$ is in error by $\pm$ 0.033 **M** for the example described in the text.

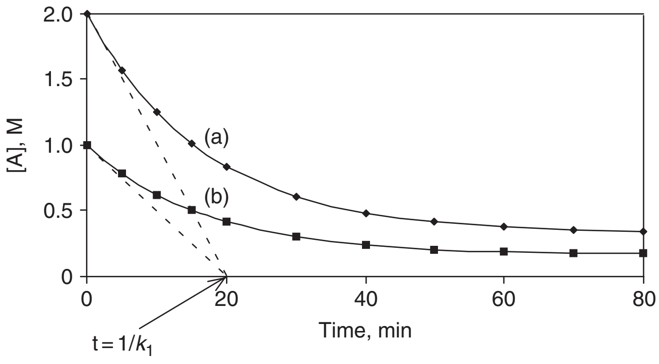


FIGURE 2.10 Variation in [A] for a reversible first-order reaction for which $k_1 =$ 0.050 min^{-1} and $k_{-1} = 0.010$ min^{-1}. Curve (a) corresponds to $[A]_o = 2.00$ **M** and curve (b) corresponds to $[A]_o = 1.00$ **M**. Note that the initial rates extrapolate to a value of $1/k_1$.

when the initial concentration of A is varied in a series of experiments. Figure 2.10 shows the variation in [A] for the cases where $[A]_o = 1.00$ **M** and $[A]_o = 2.00$ **M** when $k_1 = 0.050$ min^{-1}, $k_{-1} = 0.010$ min^{-1}, and K = 5.00. When $[A]_o = 1.00$ **M**, $[A]_f = 0.167$ **M**, but when $[A]_o = 2.00$ **M**, $[A]_f = 0.333$ **M**. However when the tangents are drawn for the two rate plots to indicate the initial rates, it is seen that they both have abscissa values of $1/k_1$, which is equal to 20 min, and the correct value $k_1 = 0.050$ min^{-1}.

The initial rate of the reaction can be represented as

$$-\frac{d[A]}{dt} = k_1[A]_o - k_{-1}[B]_o \tag{2.138}$$

However, in the example being considered, no B is initially present, so we can omit the last term on the right-hand side and write the equation to be integrated as

$$-\int_{[A]_o}^{[A]} d[A] = k_1[A]_o \int_0^t dt \tag{2.139}$$

When the integration is performed, we obtain

$$[A]_o - [A] = k_1[A]_o t \tag{2.140}$$

At the beginning of the reaction, $[A] = 0$, so Eq. (2.140) reduces to

$$[A]_o = k_1[A]_o t \tag{2.141}$$

Solving for t we find that

$$t = \frac{1}{k_1} \tag{2.142}$$

Therefore, it is apparent that the extrapolation of the initial rate to a concentration of zero to determine the intercept on the time axis yields a line that intersects the axis at a value of $1/k_1$. The intercept is independent of the initial concentration of A. This technique provides a convenient way to determine k_1 for the reaction.

The problem of reactions that do not go to completion is a frequently occurring one. We have shown here only the mechanics of dealing with a reversible system in which the reaction in each direction is first-order. Other cases that might arise are reversible second-order reactions, series reactions in which only one step is reversible, etc. These cases are quite complicated mathematically, and their treatment is beyond the scope of this book. However, many such systems have been elegantly described (see, for example, Schmid and Sapunov, 1982). The interested reader is directed to these worked-out exercises in applied mathematics for more details.

2.7 AUTOCATALYSIS

For certain reactions, it is observed that the rate of the reaction increases as the reaction progresses. Such a situation occurs when a product acts as a catalyst for the reaction. Suppose the reaction

$$A \rightarrow B \tag{2.143}$$

is first-order in A but that the reaction is catalyzed by B. As B is formed, the rate of the reaction will increase, and the first-order plot will deviate from linearity with the slope of the line *increasing* in magnitude as shown in Figure 2.11.

Mathematically, this system can be described by the rate law

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}] \tag{2.144}$$

Because of the stoichiometry of the reaction shown, the concentration of A reacted is equal to the concentration of B produced, so that

$$[\mathrm{A}]_o - [\mathrm{A}] = [\mathrm{B}] - [\mathrm{B}]_o \tag{2.145}$$

Therefore, the concentration of B can be expressed as

$$[\mathrm{B}] = [\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}] \tag{2.146}$$

and when this value is substituted into Eq. (2.144), we obtain

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]([\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}]) \tag{2.147}$$

This equation can be written as

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]([\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}])} = k\ dt \tag{2.148}$$

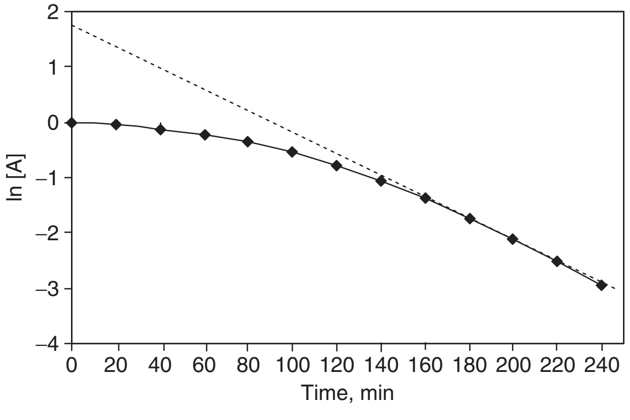


FIGURE 2.11 A plot of ln[A] vs. time for the autocatalytic process A → B. Conditions are $[\mathrm{A}]_o = 1.00\,\mathbf{M}$, $[\mathrm{B}]_o = 0.100\,\mathbf{M}$, and $k = 0.020\ \mathrm{min}^{-1}$.

It should be apparent that this equation is very similar to that for the second-order mixed rate law shown in Eq. (2.6). Following the procedure illustrated in that case, separating the fractions gives

$$\frac{1}{[\mathrm{A}]([\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}])} = \frac{C_1}{[\mathrm{A}]} + \frac{C_2}{[\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}]} \tag{2.149}$$

Therefore, by obtaining a common denominator on the right-hand side, we have

$$\frac{C_1}{[\mathrm{A}]} + \frac{C_2}{[\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}]} = \frac{C_1([\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}]) + C_2[\mathrm{A}]}{[\mathrm{A}]([\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}])} \tag{2.150}$$

By comparing Eqs. (2.149) and (2.150), we see that

$$C_1([\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}]) + C_2[\mathrm{A}] = 1 \tag{2.151}$$

Expanding this expression yields

$$C_1[\mathrm{A}]_o + C_1[\mathrm{B}]_o - C_1[\mathrm{A}] + C_2[\mathrm{A}] = 1 \tag{2.152}$$

When A has reacted completely so that $[\mathrm{A}] = 0$, this equation reduces to

$$C_1[\mathrm{A}]_o + C_1[\mathrm{B}]_o = 1 \tag{2.153}$$

because

$$C_2[\mathrm{A}] - C_1[\mathrm{A}] = 0 \tag{2.154}$$

During most of the reaction, [A] is not equal to zero. Therefore, from Eq. (2.144) we see that $C_1 = C_2$. Therefore,

$$C_1([\mathrm{A}]_o + [\mathrm{B}]_o) = 1 \tag{2.155}$$

which enables us to write

$$C_1 = \frac{1}{([\mathrm{A}]_o + [\mathrm{B}]_o)} = C_2 \tag{2.156}$$

Substituting for C_1 and C_2 in the partial fractions yields

$$-\left[\frac{d[\mathrm{A}]}{[\mathrm{A}]([\mathrm{A}]_o + [\mathrm{B}]_o)} + \frac{d[\mathrm{A}]}{([\mathrm{A}]_o + [\mathrm{B}]_o)([\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}])}\right] = k\,dt \tag{2.157}$$

This equation can be integrated to obtain

$$\frac{1}{[\mathrm{A}]_o + [\mathrm{B}]_o}\ln\frac{[\mathrm{A}]_o}{[\mathrm{A}]} + \frac{1}{[\mathrm{A}]_o + [\mathrm{B}]_o}\ln\frac{[\mathrm{A}]_o + [\mathrm{B}]_o - [\mathrm{A}]}{[\mathrm{B}]_o} = kt \tag{2.158}$$

Upon substituting $[B] = [A]_o + [B]_o - [A]$ and simplifying, one obtains

$$\frac{1}{[A]_o + [B]_o} \ln \frac{[A]_o[B]}{[B]_o[A]} = kt \tag{2.159}$$

This equation can be rearranged to give

$$\ln \frac{[A]_o[B]}{[B]_o[A]} = ([A]_o + [B]_o)kt \tag{2.160}$$

which can be written in exponential form as

$$\frac{[A]_o[B]}{[B]_o[A]} = e^{([A]_o+[B]_o)kt} \tag{2.161}$$

We now want to find the expression that gives the concentration of B as a function of time. From the stoichiometry of the reaction, we know that

$$[A] = [A]_o + [B]_o - [B] \tag{2.162}$$

Substituting for [A] in Eq. (2.161) and multiplying both sides of the equation by $[B]_o$ gives

$$\frac{[A]_o[B]}{[A]_o + [B]_o - [B]} = [B]_o e^{([A]_o+[B]_o)kt} \tag{2.163}$$

This equation can be expanded to obtain

$$[A]_o[B] = [A]_o[B]_o e^{([A]_o+[B]_o)kt} + [B]_o^2 e^{([A]_o+[B]_o)kt} - [B][B]_o e^{([A]_o+[B]_o)kt} \tag{2.164}$$

Rearranging and solving for [B] gives

$$[B] = \frac{[A]_o[B]_o e^{([A]_o+[B]_o)kt} + [B]_o^2 e^{([A]_o+[B]_o)kt}}{[B]_o e^{([A]_o+[B]_o)kt} + [A]_o} \tag{2.165}$$

Dividing each term in the numerator and denominator by $[B]_o \exp(([A]_o + [B]_o)kt)$ gives the desired expression for [B] as a function of time.

$$[B] = \frac{[A]_o + [B]_o}{1 + \dfrac{[A]_o}{[B]_o} e^{-([A]_o+[B]_o)kt}} \tag{2.166}$$

We now seek an expression that gives the variation in concentration of A with time. By substituting $[A]_o + [B]_o - [A]$ for [B] in Eq. (2.161) we obtain

$$\frac{[\mathrm{A}]_\mathrm{o}[\mathrm{B}]}{[\mathrm{B}]_\mathrm{o}[\mathrm{A}]} = \mathrm{e}^{([\mathrm{A}]_\mathrm{o}+[\mathrm{B}]_\mathrm{o})kt} = \frac{[\mathrm{A}]_\mathrm{o}([\mathrm{A}]_\mathrm{o} + [\mathrm{B}]_\mathrm{o} - [\mathrm{A}])}{[\mathrm{B}]_\mathrm{o}[\mathrm{A}]} \tag{2.167}$$

Carrying out the multiplication on the right-hand side of this equation gives

$$\frac{[\mathrm{A}]_\mathrm{o}[\mathrm{B}]}{[\mathrm{B}]_\mathrm{o}[\mathrm{A}]} = \mathrm{e}^{([\mathrm{A}]_\mathrm{o}+[\mathrm{B}]_\mathrm{o})kt} = \frac{[\mathrm{A}]_\mathrm{o}^2 + [\mathrm{A}]_\mathrm{o}[\mathrm{B}]_\mathrm{o} - [\mathrm{A}]_\mathrm{o}[\mathrm{A}]}{[\mathrm{B}]_\mathrm{o}[\mathrm{A}]} \tag{2.168}$$

Therefore,

$$[\mathrm{B}]_\mathrm{o}[\mathrm{A}]\mathrm{e}^{([\mathrm{A}]_\mathrm{o}+[\mathrm{B}]_\mathrm{o})kt} = [\mathrm{A}]_\mathrm{o}^2 + [\mathrm{A}]_\mathrm{o}[\mathrm{B}]_\mathrm{o} - [\mathrm{A}]_\mathrm{o}[\mathrm{A}] \tag{2.169}$$

By rearranging, we obtain

$$[\mathrm{B}]_\mathrm{o}[\mathrm{A}]\mathrm{e}^{([\mathrm{A}]_\mathrm{o}+[\mathrm{B}]_\mathrm{o})kt} - [\mathrm{A}]_\mathrm{o}^2 - [\mathrm{A}]_\mathrm{o}[\mathrm{B}]_\mathrm{o} + [\mathrm{A}]_\mathrm{o}[\mathrm{A}] = 0 \tag{2.170}$$

Solving for [A] gives

$$[\mathrm{A}] = \frac{[\mathrm{A}]_\mathrm{o}^2 + [\mathrm{B}]_\mathrm{o}[\mathrm{A}]_\mathrm{o}}{[\mathrm{A}]_\mathrm{o} + [\mathrm{B}]_\mathrm{o}\mathrm{e}^{([\mathrm{A}]_\mathrm{o}+[\mathrm{B}]_\mathrm{o})kt}} \tag{2.171}$$

Dividing each term in the numerator and denominator by $[\mathrm{A}]_\mathrm{o}$ yields the equation in the form most often encountered.

$$[\mathrm{A}] = \frac{[\mathrm{A}]_\mathrm{o} + [\mathrm{B}]_\mathrm{o}}{1 + \dfrac{[B]_o}{[\mathrm{A}]_\mathrm{o}} e^{([\mathrm{A}]_\mathrm{o}+[\mathrm{B}]_\mathrm{o})kt}} \tag{2.172}$$

Having derived equations for the concentrations of A and B for an autocatalytic reaction, we should now display the results in graphical form. Figure 2.12 shows the variation of [A] and [B] for a reaction where $[\mathrm{A}]_\mathrm{o} = 1.00\,\mathbf{M}$, $[\mathrm{B}]_\mathrm{o} = 0.100\,\mathbf{M}$, and $k = 0.020\ \mathrm{min}^{-1}$. The sigmoidal nature of the curves, which is characteristic of autocatalytic processes, is clearly visible. The nature of the curves suggests that the rate goes through a maximum at some concentration of A and then decreases as the concentration of A decreases.

It is of interest to note that a plot of ln[A] versus t shows first-order behavior at longer times even though the overall plot is curved. Figure 2.11 shows this behavior for a hypothetical case using the same concentration data used to prepare Figure 2.12. From such a plot, it is possible to evaluate k from data at longer reaction times, as is also shown in Figure 2.11 where the slope is $-k([\mathrm{A}]_\mathrm{o} + [\mathrm{B}]_\mathrm{o})$.

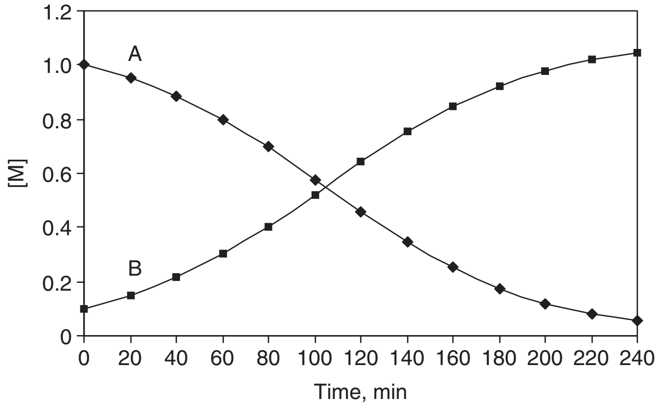


FIGURE 2.12 Concentration of A and B for the autocatalytic process A → B. Conditions are $[A]_o = 1.00\,\mathbf{M}$, $[B]_o = 0.100\,\mathbf{M}$, and $k = 0.020\ \text{min}^{-1}$.

2.8 EFFECT OF TEMPERATURE

In Chapter 1, the effect of temperature on reaction rate was illustrated by means of the Arrhenius equation. In most cases, a reaction can be studied conveniently over a rather narrow range of temperature, perhaps 30 to 40°C. Over a range of temperature of that magnitude, it is normal for a plot of ln k versus 1/T to be linear. However, for a very wide range of temperature, such a plot will not be linear, as will now be shown.

If we consider the Arrhenius equation,

$$k = A\mathrm{e}^{-E_a/RT} \tag{2.173}$$

we can see that the relationship between ln k and temperature cannot be linear over a large range of temperatures. For example, if the activation energy is 100 kJ/mol and the temperature is 1000 K, k would have a value of about 6×10^{-6} A. At 2000 K, k is 2.45×10^{-3} A, at 10,000 K, k would be 0.300 A, etc. It can be shown that at sufficiently high T, $k \rightarrow A$ because $RT \rightarrow \infty$ and $\mathrm{e}^{-1/RT} \rightarrow 1$. In fact, a plot of k versus T is sigmoidal, and k approaches A as an upper limit. However, in the typical temperature range over which most reactions can be studied, k increases with temperature in the way described earlier.

It is often stated as general rule that the rate of many reactions doubles for a 10°C rise in temperature. This can be examined easily by writing the

Arrhenius equation for the rate constants at two temperatures and solving for E_a, which gives

$$E_a = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{k_2}{k_1} \tag{2.174}$$

By choosing T_1 and T_2 so that they represent a 10° interval, we can evaluate $\ln(k_2/k_1)$ and hence k_2/k_1, as related to E_a. For example, if we take T_2 to be 305 K and T_1 to be 295 K and calculate k_2/k_1 for various values of E_a, we obtain the results shown in Figure 2.13. It is obvious that $k_2/k_1 = 2$ (which means that the rate doubles) *only* if the activation energy is about 50 kJ/mol. On the other hand, if E_a is about 150 kJ/mol, $k_2/k_1 = 7.4$ if the temperature is increased from 295 to 305 K.

This behavior suggests that it would be of interest to examine the relationship between E_a, k_2/k_1, and the temperature interval, because both E_a and the temperature where the 10° range occurs affect the values of k_2/k_1. Equation (2.174) can be written as

$$\frac{E_a(T_2 - T_1)}{R} = T_1T_2 \ln \frac{k_2}{k_1} \tag{2.175}$$

For a specified value of E_a and with T_1 and T_2 chosen so that $T_2 - T_1$ is 10 K, the left-hand side of Eq. (2.175) is constant, and hyperbolas result when $\ln(k_2/k_1)$ is plotted against T_1T_2. In Figure 2.14, curves are shown that are obtained when k_2/k_1 is plotted versus the average temperature in a 10° interval for activation energies of 50, 75, and 100 kJ/mol. It is clear

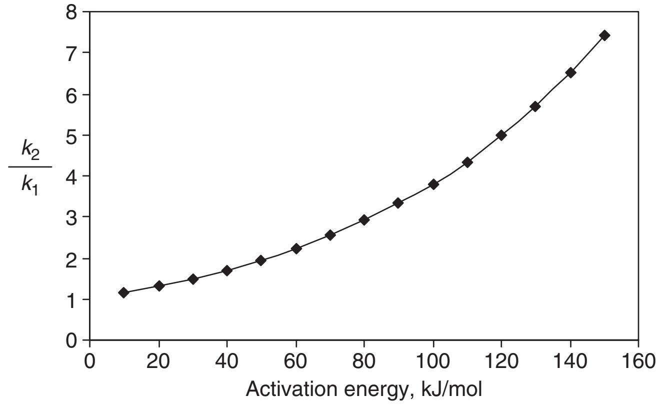


FIGURE 2.13 The effect of a temperature increase from 295 to 305 K on the ratio of k_2/k_1.

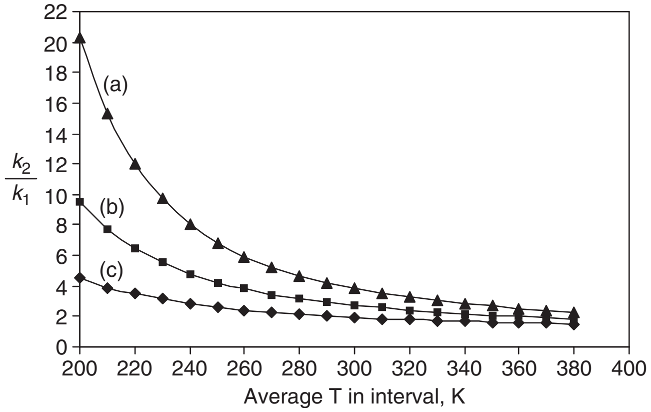


FIGURE 2.14 The effect of a 10 degree rise in temperature on k_2/k_1 for different activation energies. Curves (a), (b), and (c) correspond to activation energies of 100, 75, and 50 kJ/mol, respectively.

from this figure that k_2/k_1 has a value of 2 at different temperatures depending on the activation energy. At 300 K (the interval of 295–305 K), k_2/k_1 is approximately 2 only when the activation energy is 50 kJ/mol, but it is approximately 3 if the activation energy is 75 kJ/mol, and it is approximately 4 if the activation energy is 100 kJ/mol. At intervals involving lower average temperatures, the effect is much greater, while for intervals involving higher temperatures, the effect is much less. In any event, this analysis shows that the assumption that the rate doubles for a 10° rise in temperature is of limited usefulness.

The effect of temperature on reaction rate was first observed over 100 years ago by Hood who noted that the relationship could be written as

$$\log k = \frac{-A}{\mathrm{T}} + B \tag{2.176}$$

where A and B are constants. This equation can also be written using natural logarithms in the form

$$\ln k = \ln A - \frac{E_\mathrm{a}}{\mathrm{RT}} \tag{2.177}$$

which we recognize as a form of the Arrhenius equation.

For a system involving chemical equilibrium,

$$\frac{d \ln \mathrm{K}}{d\mathrm{T}} = \frac{\Delta \mathrm{E}}{\mathrm{RT}^2} \tag{2.178}$$

Consider the chemical reaction represented as

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{2.179}$$

At equilibrium, the rates of the forward and reverse reactions are equal, so we can write

$$k_1[A][B] = k_{-1}[C][D] \tag{2.180}$$

Therefore, the equilibrium constant for the reaction can be written as

$$K = \frac{k_1}{k_{-1}} = \frac{[C][D]}{[A][B]} \tag{2.181}$$

Substituting this result into Eq. (2.178) gives

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{\Delta E}{RT^2} \tag{2.182}$$

From this equation, the effect of temperature on the forward reaction is expressed as

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \tag{2.183}$$

where E_1 is the energy of the reaction in the forward direction while the effect of temperature on the reverse reaction is given by

$$\frac{d \ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2} \tag{2.184}$$

where E_{-1} is the energy of the reaction in the reverse direction. However, the overall energy change for the reaction is

$$\Delta E = E_1 - E_{-1} \tag{2.185}$$

The relationship between the energies involved is illustrated in Figure 2.15. As was shown in Chapter 1, a plot of ln k vs. $1/T$ is linear with a slope of $-E_a/R$. However, for reactions that are studied over a very large range of temperature, the plots are not exactly linear as described earlier.

For some reactions, the frequency factor is also a function of temperature, which is usually represented by a factor of T^n in the Arrhenius equation.

$$k = A\ T^n\ e^{-E_a/RT} \tag{2.186}$$

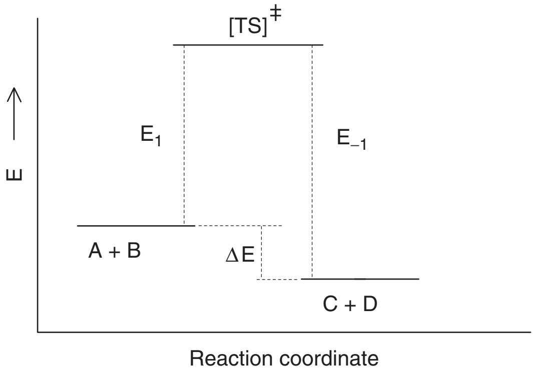


FIGURE 2.15 Energy relationships for the reaction A + B → C + D. The transition state is denoted as $[TS]^{\ddagger}$.

In most cases, n is an integer or a half-integer (see Chapter 4). Therefore, a more complete but less frequently used equation representing the rate constant as a function of temperature is

$$\ln k = \ln A + n \ln \mathrm{T} - \frac{E_a}{\mathrm{RT}} \tag{2.187}$$

The interpretation of E_1,E_{-1}, and ΔE is shown graphically in Figure 2.14. In this case, the activation energy for the forward reaction is E_1 while that for the reverse reaction is E_{-1}. From thermodynamics, we know that

$$\ln \mathrm{K} = \frac{-\Delta \mathrm{G}}{\mathrm{RT}} = \frac{-\Delta \mathrm{H}}{\mathrm{RT}} + \frac{\Delta \mathrm{S}}{\mathrm{R}} \tag{2.188}$$

Writing a similar equation of this form for both the forward and reverse reaction and combining them with Eq. (2.178) enables us to show that*

$$\Delta \mathrm{H} = \mathrm{E}_1 - \mathrm{E}_{-1} \tag{2.189}$$

Since the equilibrium constant for a reaction is related to ΔG by the equation

$$\Delta \mathrm{G} = -\mathrm{RT} \ln \mathrm{K} \tag{2.190}$$

we can write

$$\mathrm{K} = e^{-\Delta \mathrm{G}/\mathrm{RT}} \tag{2.191}$$

*For details, see S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1960, pp. 70–72. Note that Benson uses a mixture of subscripts in his Eq. (IV.3A.5), which makes it somewhat unclear what energies are involved.

By analogy, for the forward reaction we can write

$$k_1 = A_1 e^{-\Delta G_1^\ddagger/RT} \tag{2.192}$$

and

$$k_{-1} = A_{-1} e^{-\Delta G_{-1}^\ddagger/RT} \tag{2.193}$$

for the reverse reaction. In these relationships, $\Delta G_1^\ddagger$ and $\Delta G_{-1}^\ddagger$ are the free energies of the formation of the transition state from the reactants and products, respectively. We will assume that the transition state is the same regardless of which direction the reaction takes place, which is often referred to as the *principle of microscopic reversibility*. In such a case, it is generally assumed that $A_1 = A_{-1}$, and the difference in rates of the forward and reverse reactions is due only to the difference in $\Delta G^\ddagger$ values. Therefore,

$$\frac{k_1}{k_{-1}} = e^{\frac{\Delta S_1^\ddagger - \Delta S_{-1}^\ddagger}{R}} e^{\frac{-\Delta H_1^\ddagger + \Delta H_{-1}^\ddagger}{RT}} \tag{2.194}$$

Kinetic studies are generally more concerned with the forward reaction, for which

$$k_1 = A_1 e^{\frac{\Delta S_1^\ddagger}{R}} e^{-\frac{\Delta H_1^\ddagger}{RT}} \tag{2.195}$$

Written in logarithmic form, this equation becomes

$$\ln k_1 = \ln A_1 + \frac{\Delta S_1^\ddagger}{R} - \frac{\Delta H_1^\ddagger}{RT} \tag{2.196}$$

This equation is known as the Eyring equation. When ln k is plotted versus $1/T$, a line is obtained having a slope of $-\Delta H^\ddagger/R$. Once $\Delta H^\ddagger$ is known, $\Delta S^\ddagger$ can be calculated by means of this equation. The entropy of activation is a useful property that is based on the choice of standard states. For a gas phase reaction in which a molecule X–Y dissociates, $\Delta S^\ddagger$ would be expected to be positive. However, if the reaction takes place in solution and if the solvent is polar, dissociation of X–Y into X^+ and Y^- followed by solvation of the ions could result in $\Delta S^\ddagger$ being negative. It should be noted that Eq. (2.194) applies strictly only to first-order processes. For applications to other reaction orders, see R. Schmid and V. N. Sapunov, *Non-formal Kinetics*, Verlag Chemie, Weinheim, 1982, p. 110. We will have more to say in later chapters about the effects of temperature and solvation on reaction rates.

Although several reaction schemes have been described in this chapter, there are many more that can be devised. The mathematics of many of those systems can be found in particular in the books by Benson, Emanuel and Knorre, and Schmid and Sapunov.

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PROBLEMS

1. The reaction of $NO(g)$ with $Br_2(g)$ is believed to take place in two steps:

$$NO(g) + Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ONBr_2(g) \quad \text{(fast)}$$

$$ONBr_2(g) + NO(g) \xrightarrow{k_2} 2\ ONBr(g) \quad \text{(slow)}$$

The $ONBr_2(g)$ produced in the first step is unstable. On the basis of this information, write the rate law expected for the reaction. Obtain the rate law describing the concentration of $ONBr_2(g)$ with time and derive the final rate law for the reaction.

2. The reaction A $\rightarrow$ P produces the following data.

Time, min	0	20	40	60	80	100	120
[A], **M**	0.800	0.709	0.557	0.366	0.207	0.096	0.042

Plot [A] vs. time and tell as much as you can about the mechanism of the reaction from the nature of the graph. Now determine the rate law for the reaction and evaluate the rate constant(s).

3. For the reacting system $X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y$ the following data were obtained when no Y was present initially and two starting concentrations of X were used.

Time, hr	0	10	20	30	40	50	60
[X], **M**	0.600	0.374	0.250	0.182	0.145	0.125	0.113
[X], **M**	1.200	0.750	0.501	0.365	0.290	0.250	0.227

Write the rate equation for the change in [X] with time. Make appropriate substitutions and determine the final rate equation and then integrate it. Use the preceding data to determine k_1.

4. Suppose a dimer, A_2, reacts by first dissociating into monomers, then it is transformed into B.

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A \overset{k_2}{\rightleftharpoons} B$$

Assume that a steady-state concentration of A is maintained and derive the expression for the rate of disappearance of A_2. Integrate this expression to obtain the integrated rate law.

5. ^{64}Cu undergoes radioactive decay by β^+ emission to produce ^{64}Zn and β^- emission to produce ^{64}Ni electron capture simultaneously. If the half-life of ^{64}Cu is 12.8 years, obtain an expression for the amounts of ^{64}Zn and ^{64}Ni at any time, *t*.

6. ^{38}S decays by β^- emission to ^{38}Cl with a half-life 2.87 hrs. The ^{38}Cl produced decays by β^- emission to ^{38}Ar with a half-life of 37.3 min. Obtain an expression for the amount of each nuclide as a function of time.

7. In reference to Problem 6, determine the maximum number of ^{38}Cl atoms that is ever present if the original sample of ^{38}S contains 10^4 atoms.

8. Consider the elementary steps in the reaction of NO and F_2.

$$NO + F_2 \xrightarrow{k_1} ONF + F$$

$$NO + F \xrightarrow{k_2} ONF$$

Derive the rate laws that result from the conditions (a) $k_1 >> k_2$, (b) $k_2 >> k_1$, and (c) with $k_1 \approx k_2$.

9. Cadmium-117 undergoes β^- decay with a half-life of 2.4 hrs to ^{117}In, which undergoes β^- decay with a half-life of 42 min to ^{117}Sn, which is stable. (a) If a sample of initially pure ^{117}Cd contains 1.50×10^6 atoms, how many atoms will remain after 4.00 hrs? (b) How many atoms of ^{117}In will be present after 4.00 hours? (c) How many atoms of ^{117}Sn will be present after this time?

10. For a reaction that can be written as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

the value of k_1 is $5.65 \times 10^{-3}\ \text{min}^{-1}$ and the time necessary to reach the maximum concentration of B is 26 minutes. What is the value of k_2?

11. Using the data given in the text to construct Figure 2.6, calculate the time required for the intermediates B and B′ to reach maximum concentration. Explain why using these times to determine rate constants presents some difficulties.

12. Suppose a first-order reaction yields the following data:

t, °C	0	20	40	60
$10^3 \times k$, sec^{-1}	1.23	24.0	279	2730

What are the values for E_a and A? What would be the half-life for the reaction at 75°C?

13. For a the reaction

$$A + B \underset{k_1}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} C$$

(where I is an intermediate that reacts much faster than it decays to reform reactants) show that

$$\frac{d[C]}{dt} = k_2 K[A][B]$$

14. For the process

$$X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$$

plot the concentration versus time when $k_1 = 0.012\,\text{sec}^{-1}$ and $k_2 = 0.850\ \text{sec}^{-1}$ if $[X]_o = 0.750\,\mathbf{M}$ and no Y or Z is present initially. Follow the reaction over at least two or three half-lives of X. Calculate the time to the maximum concentration of Y.

15. The decomposition of X yields Y and Z as the result of first-order processes. For the disappearance of X, the following data were obtained.

Time, min	[X], M	Time, min	[X], M
0	0.860	40	0.274
10	0.635	50	0.207
20	0.484	60	0.146
30	0.365		

Write the differential equations to represent the change in the concentration of each compound with time. Solve the equation for the change in concentration of X and determine the overall rate constant. If after 30 minutes, the concentration of Y is 0.190 M and that of Z is 0.310, determine the rate constants for their formation.

CHAPTER 3

Techniques and Methods

In Chapter 2, several types of kinetic schemes were examined in detail. While the mathematical apparatus was developed to describe these cases, little was said about other methods used in kinetic studies or about experimental techniques. In this chapter, we will describe some of the methods employed in the study of kinetics that do not make use of the integrated rate laws. In some cases, the exact rate law may be unknown, and some of the experimental techniques do not make use of the classical determination of concentration as a function of time to get data to fit to a rate law. A few of the techniques described in this chapter are particularly useful in such cases.

There are available compendia that present an enormous amount of information on experimental methods for studying the kinetics of chemical reactions. One such source is Bernasconi, Editor (1986), *Investigations of Rates and Mechanisms of Reactions*, which contains two parts of the series *Techniques of Chemistry* (Weissberger, Series Editor) that presents discussions on all phases of kinetics theory and techniques. Part I, *General Considerations and Reactions at Conventional Rates*, would be especially valuable for a study of kinetic methods. Part II, *Investigation of Elementary Reaction Steps in Solution and Fast Reaction Techniques*, deals with additional aspects of solution kinetics. These reference works should be consulted for extensive discussions of kinetic methods.

3.1 CALCULATING RATE CONSTANTS

One of the traditional ways of examining data from a kinetic analysis is that of preparing a table of the results and looking for consistency. In this method, the data correlated by a particular rate law are used to calculate

the rate constant for each (concentration, time) data pair. Several rate laws can be tried, but only the *correct* rate law will give a constant value (within experimental error) for the rate constant. We can illustrate this procedure by making use of the data presented in Section 2.1 for a kinetic study of the hydrolysis of ethyl acetate with sodium hydroxide. In that experiment, the initial concentration of NaOH was 0.0100 **M** (the value of a in the second-order rate law) and the initial concentration of ethyl acetate was 0.0580 **M** (the value of b in the rate law). Therefore, $(a - b) = 0.00420$ **M** and $1/(a - b) = 238.1$. Using these values and the concentration and time data shown in Table 2.1, the results shown in Table 3.1 were obtained when a second-order rate law was used.

Several factors should be noted from the results shown in Table 3.1. First, the calculated k values for sampling times of 1 and 3 minutes deviate rather significantly from the values at longer times. This is due to the difficulties of mixing the solutions to start the reaction and then obtaining homogeneous aliquots after very short reaction times. For those two samples, the sampling time itself is a significant fraction of the measured reaction time. The data used in the calculations were obtained from a ''real'' experimental kinetics run so this was inevitable. Second, the calculated k values are essentially constant, which would suggest that a correct rate law was being used to correlate the data. If the data showed a trend toward a higher or lower value, it would indicate that the rate law being tested was not the correct one.

TABLE 3.1 Calculated Rate Constants for the Hydrolysis of Ethyl Acetate Using the Experimental Data Shown in Table 2.1.

Time, min	$\frac{(a-x)}{(b-x)}$	$\frac{b(a-x)}{a(b-x)}$	$\ln\frac{b(a-x)}{a(b-x)}$	$\frac{1}{(a-b)}\ln\frac{b(a-x)}{a(b-x)}$	k, $\mathbf{M}^{-1}$ min^{-1}
1	1.83	1.06	0.0596	14.2	14.2
3	1.90	1.10	0.0971	23.1	7.71
5	2.10	1.22	0.197	46.9	9.38
10	2.50	1.45	0.372	88.6	8.86
20	3.38	1.96	0.673	160	8.01
35	5.57	3.24	1.17	279	7.98
55	12.8	7.37	2.00	475	8.65
75	25.3	14.7	2.68	639	8.52

In Chapter 2, the data obtained from this experiment were analyzed by performing linear regression to fit the concentration and time data to a second-order rate equation. By that method, the value determined for k was 8.47 min^{-1}. Realizing that the first data point (obtained after a reaction time of only 1 minute) is in error, we can justifiably delete it from consideration. The calculated values for k (shown in the last column of Table 3.1) are otherwise consistent. Therefore, determining the average of those values should give a reliable value for k, and that average value is 8.44 min^{-1}, which is in excellent agreement with the value obtained earlier by fitting the data to the second-order rate law. It is readily apparent that the method of calculating a value for k for each data point and determining the average value can be used to determine k.

In Section 1.3, we described some of the difficulties in analyzing data where errors in the data make it difficult to determine the applicable concentration function. Using the method of calculating rate constants may make it impossible to distinguish between experimental errors in the data while graphical presentation of the data *may* reveal a trend or curvature of the plot, which *suggests* that another rate law is applicable. Finally, when the calculated rate constants are displayed as shown in Table 3.1, it is usually difficult to detect a trend in the values unless the reaction has been studied over a large fraction of reaction. In all cases where it is possible to do so, a reaction should be studied over several half-lives in order to obtain data that are amenable to kinetic analysis. The data shown in Table 3.1 indicate studying the reaction for only the first few minutes would not have made it possible to conclude much about the kinetics of the reaction.

3.2 THE METHOD OF HALF-LIVES

In Section 2.2, the equation giving the half-life as a function of reaction order and initial concentration was derived. That equation can be written in the general form

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[\mathrm{A}]_o^{\,n-1}} \tag{3.1}$$

By rearrangement, the equation can also be written as

$$t_{1/2} = \frac{1}{[\mathrm{A}]_o^{\,n-1}} \cdot \frac{2^{n-1} - 1}{(n-1)k} = \frac{1}{[\mathrm{A}]_o^{\,n-1}} f(k, n) \tag{3.2}$$

where $f(k,n)$ is the appropriate function of reaction order and rate constant. Taking the logarithm of both sides of Eq. 3.2 gives

$$\ln t_{1/2} = -(n-1)\ln[\mathrm{A}]_o + \ln f(k,n) \tag{3.3}$$

Because both k and n are constants, the last term will be a constant if the experimental conditions are not changed except for $[\mathrm{A}]_o$. Therefore, if several reactions are carried out with initial concentrations of A being $[\mathrm{A}]_o$, $[\mathrm{A}]_o/2$, $[\mathrm{A}]_o/4$, etc., and the half-life for the reaction is determined in each case, a plot of $\ln[\mathrm{A}]_o$ versus $t_{1/2}$ will yield a straight line that has a slope of $-(n-1)$, which allows n, the order of the reaction, to be determined.

If the reaction is carried out using two different $[\mathrm{A}]_o$ values, a ratio of two equations having the form of Eq. (3.1) gives

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{\dfrac{1}{([\mathrm{A}]_o{}^{n-1})_1}}{\dfrac{1}{([\mathrm{A}]_o{}^{n-1})_2}} = \frac{([\mathrm{A}]_o{}^{n-1})_2}{([\mathrm{A}]_o{}^{n-1})_1} \tag{3.4}$$

Taking the logarithm of both sides of this equation, we obtain

$$\ln\frac{(t_{1/2})_1}{(t_{1/2})_2} = \ln\frac{([\mathrm{A}]_o{}^{n-1})_2}{([\mathrm{A}]_o{}^{n-1})_1} \tag{3.5}$$

which can be written as

$$\ln(\mathrm{t}_{1/2})_1 - \ln(\mathrm{t}_{1/2})_2 = (n-1)\ln([\mathrm{A}]_o)_2 - (n-1)\ln([\mathrm{A}]_o)_1 \tag{3.6}$$

Factoring out $(n-1)$ on the right-hand side of this equation gives

$$\ln(\mathrm{t}_{1/2})_1 - \ln(\mathrm{t}_{1/2})_2 = (n-1)\{\ln([\mathrm{A}]_o)_2 - \ln([\mathrm{A}]_o)_1\} \tag{3.7}$$

This equation can be rearranged to obtain

$$\frac{\ln(t_{1/2})_1 - \ln(t_{1/2})_2}{\ln([\mathrm{A}]_o)_2 - \ln([\mathrm{A}]_o)_1} = n - 1 \tag{3.8}$$

which allows us to solve for n to obtain

$$n = \frac{\ln(t_{1/2})_1 - \ln(t_{1/2})_2}{\ln([\mathrm{A}]_o)_2 - \ln([\mathrm{A}]_o)_1} + 1 \tag{3.9}$$

This equation shows that determining the half-life of the reaction using two different initial concentrations of the reactant, A, enables the value of n to

be determined. While this quick, approximate method is valid, it is not generally as accurate as more detailed methods of data analysis because it is based on only two data points. As developed here, it applies only to reactions that obey an *n*th-order rate law in one reactant.

3.3 INITIAL RATES

For a reaction involving a single reactant, the rate, R, can generally be written as

$$R = k[\mathrm{A}]^n \tag{3.10}$$

Therefore, taking logarithm of both sides of the equation gives

$$\ln R = \ln k + n \ln [\mathrm{A}] \tag{3.11}$$

For a series of initial concentrations, the concentration of A varies with time as shown in Figure 3.1. For this illustration, the data calculated for a hypothetical reaction having $n = 1$ and a rate constant of 0.020 min^{-1} were used.

The *initial* rates are determined from the slopes of the tangents drawn at $t = 0$. From the initial rates determined from the slopes, the data shown in Table 3.2 are derived.

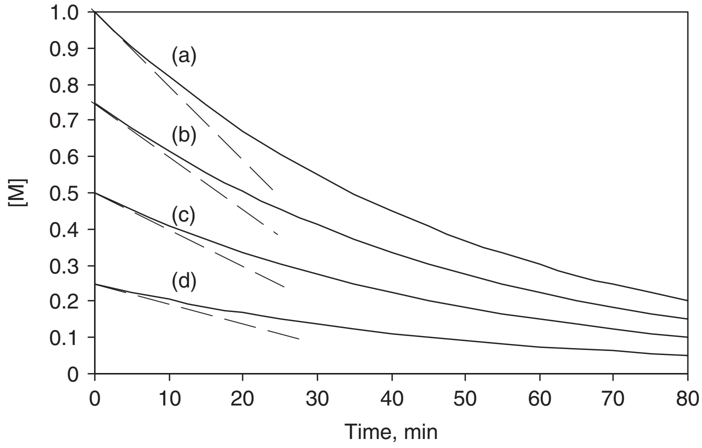


FIGURE 3.1 The method of initial rates where $[\mathrm{A}]_o$ is 1.00, 0.75, 0.50, and 0.25 **M** as represented by curves (a), (b), (c), and (d), respectively.

TABLE 3.2 Data Derived from the Method of Initial Rates Based on the Rate Plots Shown in Figure 3.1.

$[A]_o$, M	ln $[A]_o$	Initial rate, $\mathbf{M}^{-1}$ min^{-1}	ln(rate)
1.00	0.000	0.0190	−3.96
0.75	−0.288	0.0150	−4.20
0.50	−0.693	0.0101	−4.60
0.25	−1.39	0.0050	−5.30

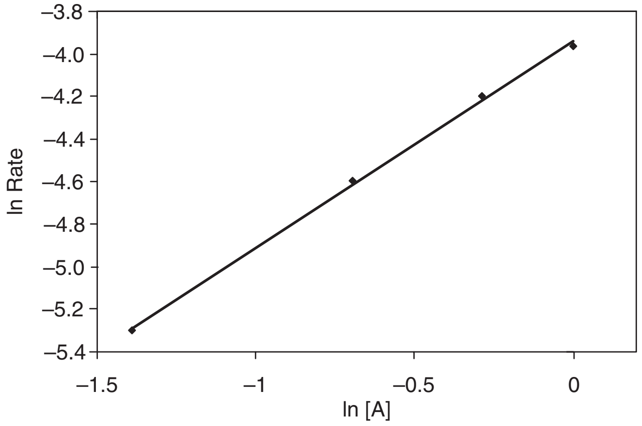


FIGURE 3.2 Plot of the logarithm of the initial rate versus the logarithm of the initial concentration.

A plot of the values obtained for ln R versus ln $[A]_o$ such as that shown in Figure 3.2 gives a linear relationship with a slope of n, the order of the reaction with respect to A. Linear regression of the preceding data, which were determined graphically from Figure 3.1, yields a slope of 0.97, which is the reaction order (within experimental error of the correct value of $n = 1$ considering that the slopes were determined graphically) and an intercept of −3.94. Since the intercept is equal to ln k, this value corresponds to a k value of 0.0195, which is sufficiently close to the value of 0.020 min^{-1} used initially in calculating the concentration as a function of time. The slight difference between the values is due to the fact that the slopes giving the initial rates were determined *graphically* by drawing tangents to the concentration versus time curves rather than by analytical

means or numerical analysis. This exercise shows that when suitable data are available, the method of initial rates can be successfully employed to determine a reaction order and rate constants.

Initial rates can also be used in another way. For example, suppose that a chemical reaction,

$$aA + bB \rightarrow \text{Products} \tag{3.12}$$

follows a rate law that can be written in terms of concentrations as

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^n[B]^m \tag{3.13}$$

If the reaction is carried out using known initial concentrations of A and B, the initial rate can be determined graphically as shown in Figure 3.1. This procedure is used to determine the *initial rate*, $(-d[A]/dt)_i$, which can be represented as

$$-\left(\frac{d[A]}{dt}\right)_{i_1} = k[A]_o{}^n[B]_o{}^m \tag{3.14}$$

In this equation, the subscript 1 indicates that this is the first of a series of experiments that are carried out using different initial concentrations of the reactants. Subsequently, the process can be repeated using different initial concentrations of A and B. For convenience in the second experiment, the initial concentrations of A and B will be taken as twice what they were in the first experiment so that $2[A]_o$ and $2[B]_o$. For these new concentrations, the initial rate can be expressed as

$$-\left(\frac{d[A]}{dt}\right)_{i_2} = k(2[A]_o)^n(2[B]_o)^m \tag{3.15}$$

Because k is a constant, a ratio of the initial rates determined for the two sets of concentrations gives

$$\frac{-\left(\frac{d[A]}{dt}\right)_{i_2}}{-\left(\frac{d[A]}{dt}\right)_{i_1}} = \frac{k(2[A]_o)^n(2[B]_o)^m}{k[A]_o{}^n[B]_o{}^m} = 2^n \times 2^m = 2^{n+m} \tag{3.16}$$

Therefore, the overall reaction order, $n + m$, can easily be determined from the initial rates measured at two different starting concentrations of reactants.

3.4 USING LARGE EXCESS OF A REACTANT (FLOODING)

For a reaction that can be represented by Eq. (3.12), the general rate law can be written as

$$-\frac{d[A]}{dt} = k[A]^n[B]^m \tag{3.17}$$

If the concentration of B is made very high with respect to that of A, the concentration of B will not change significantly while the concentration of A changes by an amount that can be represented as x. Therefore, the rate law can be represented as

$$-\frac{d[A]}{dt} = \frac{dx}{dt} = k([A]_o - x)^n[B]^m \tag{3.18}$$

Since B is essentially a constant, we can write

$$\frac{dx}{dt} = k'([A]_o - x)^n \tag{3.19}$$

where k' is the actual rate constant times the concentration of B to some power, m, the order of the reaction with respect to B. This rate law can be treated by the integral methods that were described in Chapter 2 to determine n. The procedure can be repeated by making the initial concentration of A large compared to $[B]_o$ so that m can be determined. Flooding is essentially making the conditions of the reaction such that it becomes a pseudo nth-order process in one reactant by using a larger concentration of the other reactant.

Many reactions that take place in aqueous solutions or those in which H^+ or OH^- is a reactant are representative of the conditions just described. For example, in Chapter 1 the reaction of $t-(CH_3)_3CBr$ with OH^- in basic solution was described. Under these conditions, the concentration of OH^- is sufficiently large that the reaction appears to be first order in $t-(CH_3)_3CBr$, but is actually a pseudo first-order process. Many hydrolysis reactions appear to be independent of $[H_2O]$ only because water is usually present in such a large excess. Of course, not all reactions can be studied by the method of flooding because a very large excess of a reactant may cause the reaction to take place in a different way.

3.5 THE LOGARITHMIC METHOD

Suppose a reaction can be represented as

$$a\mathrm{A} + b\mathrm{B} \rightarrow \text{Products} \tag{3.20}$$

and that it follows a rate law that can be written in the form

$$\text{Rate} = k[\mathrm{A}]^n[\mathrm{B}]^m \tag{3.21}$$

If the reaction is carried out at two initial concentrations of A but with the initial concentration of B kept constant, the ratio of the reaction rates will be given by

$$\frac{R_1}{R_2} = \frac{k[\mathrm{A}]_1^n}{k[\mathrm{A}]_2^n} \tag{3.22}$$

Taking the logarithms (either natural or common) of both sides of the equation gives

$$\log\frac{R_1}{R_2} = n\log\frac{[\mathrm{A}]_1}{[\mathrm{A}]_2} \tag{3.23}$$

Solving for n gives

$$n = \frac{\log\dfrac{R_1}{R_2}}{\log\dfrac{[\mathrm{A}]_1}{[\mathrm{A}]_2}} \tag{3.24}$$

This procedure can be repeated with the initial concentration of A kept constant to determine m in a similar way by varying the initial concentration of B.

A somewhat better way to apply the logarithmic method is to carry out the reaction using several different starting concentrations of A while keeping the concentration of B constant. After determining the rates, a graph can be made of the points obtained from the ratios R_i/R_{i+1} and $[\mathrm{A}]_1/[\mathrm{A}]_{i+1}$. Taking logarithms of the ratios gives

$$\log\frac{R_i}{R_{i+1}} = n\log\frac{[\mathrm{A}]_i}{[\mathrm{A}]_{i+1}} \tag{3.25}$$

The slope of a plot of $\log(R_i/R_{i+1})$ versus $\log([\mathrm{A}]_i/[\mathrm{A}]_{i+1})$ will be equal to n, the order of the reaction with respect to A. The procedure can be repeated to find m, the order of the reaction with respect to B.

The reaction between peroxydisulfate and iodide ions can be written as

$$S_2O_8^{2-} + 3\ I^- \rightarrow I_3^- + 2\ SO_4^{2-} \tag{3.26}$$

This reaction is an interesting one because the rate law is not that which would be indicated by the coefficients in the balanced equation. It can be studied kinetically by monitoring the production of I_3^-, which gives the familiar blue color with starch as an indicator. Because I_3^- oxidizes $S_2O_3^{2-}$ by the reaction

$$I_3^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_2O_6^{2-} \tag{3.27}$$

the amount of I_3^- produced can be determined by reacting it with a known concentration of $S_2O_3^{2-}$. When the $S_2O_3^{2-}$ is exhausted, the I_3^- that is produced by I^- reacting with $S_2O_8^{2-}$ interacts with the starch to produce a blue color. In this way, the amount of I_3^- produced can be monitored, which makes it possible to determine in an indirect way the amount of $S_2O_8^{2-}$ that has reacted.

This reaction can be used to illustrate the application of the logarithmic method. In the study described here, the first of three runs had an initial concentration of $S_2O_8^{2-}$ and I^- of 0.050 **M**. The initial rate of consumption of $S_2O_8^{2-}$ was found to be 4.4×10^{-5}**M** sec^{-1}. In the second run, the concentration of $S_2O_8^{2-}$ was 0.050 **M** while that of I^- was 0.100 **M**. In this case, the initial rate of disappearance of $S_2O_8^{2-}$ was 8.6×10^{-5}**M** sec^{-1}. In the final run, the concentration of $S_2O_8^{2-}$ was 0.100 **M** while the concentration of I^- was 0.050 **M**, and the initial rate of $S_2O_8^{2-}$ loss was 8.9×10^{-5}**M** sec^{-1}. Using Eq. (3.24) we find that the data from the first and third runs where $[S_2O_8^{2-}]$ was varied gives

$$n = \frac{\log\dfrac{4.4 \times 10^{-5}}{8.9 \times 10^{-5}}}{\log\dfrac{0.050}{0.100}} = \frac{-0.306}{-0.301} = 1.0 \tag{3.28}$$

which indicates that the reaction is first-order with respect to $S_2O_8^{2-}$. If we now use the first and second runs where $[I^-]$ was varied, we find that

$$m = \frac{\log\dfrac{4.4 \times 10^{-5}}{8.6 \times 10^{-5}}}{\log\dfrac{0.050}{0.100}} = \frac{-0.291}{-0.301} = 0.97 \tag{3.29}$$

which indicates that the reaction is also first-order respect to I^- within experimental error. Consequently, we can conclude that the reaction is first-order in $S_2O_8^{2-}$ and I^-, which reinforces the conclusion that the rate

law must be deduced experimentally, not from the balancing coefficients of the equation for the reaction. Having determined the rate law, the rate constant can be found from the experimental rates at known concentrations to be equal to $1.7 \times 10^{-2}\mathbf{M}\ \mathrm{sec}^{-1}$ by means of Eq. (3.21). In this example, exactly doubling the concentrations makes it possible to deduce the reaction order by inspection, but the method described is a general one that can be applied under other conditions.

3.6 EFFECTS OF PRESSURE

Thermodynamically, pressure multiplied by volume has the dimensions of work or energy. Consequently, the application of pressure to a chemical system is equivalent to performing work on the system in a manner that is somewhat analogous to changing the temperature of the system. The principle of Le Chatelier enables us to predict the effects of changing conditions on a system at equilibrium. For example, increasing the temperature causes the system to shift in the endothermic direction. Likewise, increasing the pressure on a system at equilibrium causes the system to shift in the direction corresponding to smaller volume.

For chemical reactions, we have repeatedly assumed that a small but essentially constant concentration of the transition state is in equilibrium with the reactants. It is the concentration of the transition state that determines the magnitude of the rate constant. In Section 2.8, we dealt with the effects of temperature on the rate constant, but it should also be apparent that pressure can affect the value of k if the transition state occupies a different volume than that of the reacting species. If the transition state occupies a smaller volume than the reactants, increasing the pressure will shift the equilibrium toward the formation of a higher concentration of the transition state, which will increase the rate of the reaction. If the transition state occupies a larger volume than the reactants, increasing the pressure will decrease the concentration of the transition state and decrease the rate of the reaction. As will be discussed in Chapter 5, the effect of *internal* pressure caused by the solvent affects the rate of a reaction in much the same way as does the *external* pressure.

For a process that takes place in a solution at constant temperature, we can write the thermodynamic relationship

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{3.30}$$

where V is the partial molar volume. For a chemical reaction, the free energy of activation, $\Delta G^{\ddagger}$ can be written as

$$\Delta G^{\ddagger} = G^{\ddagger} - \Sigma G_{R} \tag{3.31}$$

where $G^{\ddagger}$ is the free energy of the transition state and ΣG_{R} represents the sum of the molar free energies of the reactants. Since the *volume of activation,* $\Delta V^{\ddagger}$, is given by

$$\Delta V^{\ddagger} = V^{\ddagger} - \Sigma V_{R} \tag{3.32}$$

(where $V^{\ddagger}$ is the volume of the transition state and ΣV_{R} is the sum of the molar volumes of the reactants), we can express the change in free energy with pressure at constant temperature as

$$\left(\frac{\partial G^{\ddagger}}{\partial P}\right)_{T} = V^{\ddagger} - \Sigma V_{R} = \Delta V^{\ddagger} \tag{3.33}$$

Strictly speaking, the concentrations of reactants should be represented in units that are independent of the changes in volume that are produced by changing the pressure. Because volumes of liquids change slightly due to their compressibility, molality or mole fraction should be chosen to measure concentrations rather than molarity. Under most conditions, the difference is negligible.

For a reaction carried out at constant temperature, we know that formation of the transition state is governed by

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{3.34}$$

where $K^{\ddagger}$ is the equilibrium constant for formation of the transition state. The equation relating the rate constant to temperature can be written as

$$\frac{\partial \ln k}{\partial T} = -\frac{E_{a}}{RT} \tag{3.35}$$

By making use of thermodynamic relationships, this equation can be transformed to give

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T} = -\frac{\Delta V^{\ddagger}}{RT} \tag{3.36}$$

Therefore, replacing the partial derivatives and solving for $V^{\ddagger}$ gives

$$\Delta V^{\ddagger} = -RT\frac{d \ln k}{dP} \tag{3.37}$$

By rearranging this equation we obtain

$$d \ln k = -\frac{\Delta V^{\ddagger}}{RT} dP \tag{3.38}$$

This equation is now in a form that allows integration, which when performed gives

$$\ln k = -\frac{\Delta V^{\ddagger}}{RT} \cdot P + C \tag{3.39}$$

where C is a constant of integration. This equation indicates that a plot of ln k versus P should be linear with a slope of $-\Delta V^{\ddagger}/RT$. Therefore, the volume of activation can be determined if the reaction is carried out to determine the rate constant at several (usually quite high) pressures. While such plots are sometimes approximately linear, they often exhibit some degree of curvature, which indicates that the value of $\Delta V^{\ddagger}$ is somewhat pressure dependent. To deal with this situation, we need either a theoretical approach to determine $\Delta V^{\ddagger}$ or perhaps a graphical procedure to obtain an empirical relationship. The latter is the usual way to determine $\Delta V^{\ddagger}$ when ln k is represented as

$$\ln k = a + bP + cP^2 \tag{3.40}$$

By combining Eqs. (3.39) and (3.40) we obtain

$$-\frac{\Delta V^{\ddagger}}{RT} P + C = a + bP + cP^2 \tag{3.41}$$

When terms involving like powers of P are equated, the result is

$$-\frac{\Delta V^{\ddagger}}{RT} P = bP \tag{3.42}$$

which indicates that

$$\Delta V^{\ddagger} = -bRT \tag{3.43}$$

It is important to have an understanding of the magnitude of the effect on the reaction that is produced by changing pressure. If we consider work done by pressure as P–V work that is expressed at constant pressure as $P\Delta V$, a change in volume of $10\,\text{cm}^3/\text{mol}$ (0.010 l/mol) by a pressure of 1000 atm would produce

$$1000\,\text{atm} \times 0.010\,\text{l/mol} = 10\ \text{l atm/mol}$$

When we recall that 1 l atm/mol = 101 J/mol, we see in this example that the work involved is only 1.01 kJ/mol. This amount of energy would be equivalent to that involving only a very small change in temperature. Therefore, in order to accomplish a change equivalent to that brought about by a modest change in temperature, an enormous change in pressure is required. As a result, pressure effects are usually determined for reactions that are studied at several kbar (1 bar = 0.98692 atm). When pressure in the range of up to 10 kbar is applied, typical $\Delta V^{\ddagger}$ values for reactions are usually in the range of approximately $\pm 25\,cm^3/mol$.

The interpretations of volumes of activation are not always unambiguous, but generally if $\Delta V^{\ddagger}$ is negative, the rate of the reaction increases as pressure is increased. This signifies that the transition state occupies a smaller volume than the reactants, and its formation is assisted by increasing the applied pressure. As a general rule, the formation of a bond (as in an associative mechanism) causes a change in $\Delta V^{\ddagger}$ of perhaps -5 to $-15\,cm^3/mol$, while the breaking of a bond (characteristic of a dissociative mechanism) causes a $\Delta V^{\ddagger}$ change of $+5$ to $+15\,cm^3/mol$. However, a bond breaking step in which ions are formed leads to a change in $\Delta V^{\ddagger}$ of as much as -20 to $-40\,cm^3/mol$. The reason for this rather large negative change is that ions are strongly solvated, which leads to a compacting and ordering of the solvent surrounding the ions. Therefore, $\Delta V^{\ddagger}$ is made up of two parts: (1) an *intrinsic* part, $\Delta V^{\ddagger}_{int}$, which depends on changes in molecular dimensions as the transition state forms and (2) a *solvation* part, $\Delta V^{\ddagger}_{solv}$, which depends on the nature and extent of solvation of the transition state. The overall volume of activation, $\Delta V^{\ddagger}$, can be expressed as the sum of these contributions,

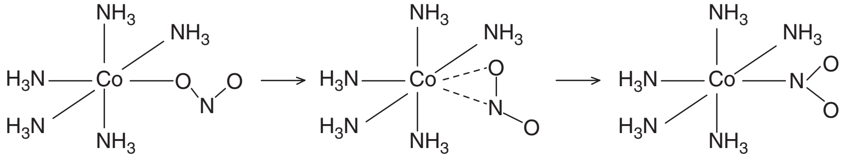
$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{int} + \Delta V^{\ddagger}_{solv} \qquad (3.44)$$

If *desolvation* occurs as the transition state is formed, $\Delta V^{\ddagger}_{solv}$ will be *positive*. If forming the transition state involves forming *ions*, $\Delta V^{\ddagger}_{solv}$ will be *negative* because of the ordering of the solvent that occurs in the vicinity of the charged ions. This phenomenon is known as *electrostriction*.

Studying the effect of pressure on the rate of a reaction can yield information about the mechanism that is difficult to obtain by any other means. One reaction in which rate studies at high pressure have yielded a considerable amount of information is a linkage isomerization reaction, which has been known for over a century. That reaction involves the different bonding modes of NO_2^- in coordination compounds and can be shown as

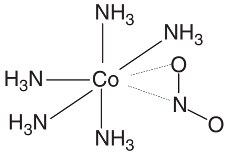
$$[Co(NH_3)_5ONO]Cl_2 \rightarrow [Co(NH_3)_5NO_2]Cl_2 \qquad (3.45)$$

This reaction has been studied thermally and photochemically both in solution and in the solid state. The reaction takes place rapidly, which is uncharacteristic of most *substitution* reactions of complexes containing Co^{3+}. A simplistic view of this process suggests that the Co–ONO bond could break and then the nitrite ion could reattach by bonding through the nitrogen atom to give Co—NO_2 linkages. The other possibility is that the Co–ONO bond may not actually break but that it merely "slides" to form the Co—NO_2 linkages.



(3.46)

Mares, Palmer, and Kelm (1978) studied the rates of linkage isomerization in $[Co(NH_3)_5ONO]^{2+}$ and the analogous Rh^{3+} and Ir^{3+} complexes under high pressure in aqueous solutions. It was reported that the linkage isomerization takes place more rapidly at high pressures. From the pressure effects on the rate constants, the volumes of activation were determined to be as follows for the complexes of the different metal ions: Co^{3+}, -6.7 ± 0.4; Rh^{3+}, -7.4 ± 0.4; Ir^{3+}, $-5.9 \pm 0.6\ cm^3/mol$. These values indicate that the transition state occupies a *smaller* volume than the reactants. This is inconsistent with a transition state involving an ion pair, $[M^{3+}\ NO_2^-]$, which would be formed by breaking the M—NO_2 bond. It is generally accepted that this reaction does not take by a bond-breaking bond-making mechanism. Furthermore, it is known that the rate of linkage isomerization in $[Co(NH_3)_5ONO]^{2+}$ is independent of the concentration of NO_2^- in the solution. This observation indicates that the coordinated NO_2^- never leaves the coordination sphere of the metal ion. Support for a structure that has NO_2^- bonded to the metal ion by both O and N atoms has been obtained by studying the reaction photochemically in the solid state and quenching the solid to very low temperature. Infrared spectra of the material shows new bands that are not characteristic of either Co–ONO or Co—NO_2 linkages but that were believed to be due to bonding in a structure like



Although we have described only one type of reaction in which the effect of pressure on the rate has been studied, there are many others. Studies of this type require specialized equipment, but they frequently yield a great deal of information about reaction mechanisms. Undoubtedly, there are many other reactions that have not been studied in this way that should be.

3.7 FLOW TECHNIQUES

When reactants are mixed, there is some finite time necessary for them to form a steady state concentration of the transition state. This time is usually very short compared to the time that the reaction is followed during a kinetic study. In this period, often called the *transient* or *pre–steady state period*, the kinetic rate laws developed earlier do not represent the reaction very well, and different experimental techniques must be employed to study such processes. One technique, developed in 1923 by Hartridge and Roughton for studying the reaction between hemoglobin and oxygen, makes use of a *continuous-flow* system. The two reacting solutions were forced under constant pressure into a mixing chamber as illustrated by the diagram shown in Figure 3.3.

After the liquids mix and the reaction starts, the mixture flows out of the mixing chamber to a point where a measuring device is located. A suitable measuring device for many reactions may be a spectrophotometer to determine the concentration of a reactant or product from absorption measurements. The length of time that the reaction has been taking place is determined by the distance from the mixing chamber to the observation point. Calculation of the reaction time is possible by making use of the flow rate of the reactants and the diameter of the tube leading from the mixing

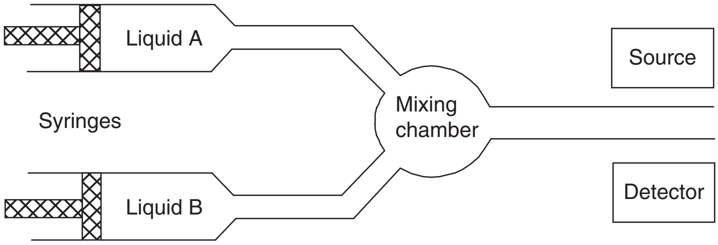


FIGURE 3.3 A schematic drawing of a continuous-flow system with the source and detector of the spectrophotometer shown.

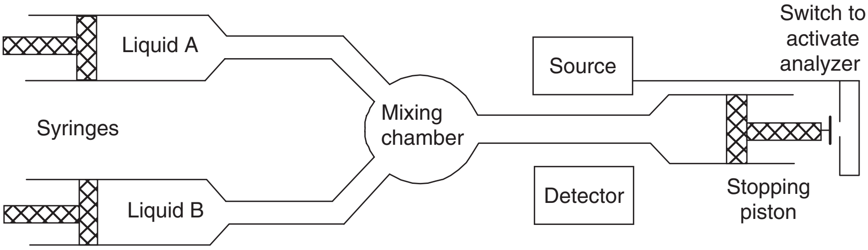


FIGURE 3.4 A schematic drawing of a stopped flow system with the source and detector of the spectrophotometer indicated.

chamber. Presently used continuous-flow systems can study reactions fast enough to have a half-life of 1 ms. Many types of flow equipment have been developed, and different methods of introducing the sample have been devised.

In the *stopped-flow* technique, the solutions are forced from syringes into a mixing chamber. After a very short period of flow, perhaps a few ms, the flow is stopped suddenly when the observation cell is filled by an opposing piston that is linked to a sensing switch that triggers the measuring device (see Figure 3.4). Small volumes of solutions are used, and the kinetic equations for modeling the reactions are equivalent to those used in conventional methods in which concentration and time are measured. Commercial stopped-flow apparatus is available with several modifications in the designs. Both stopped-flow and continuous-flow techniques are useful for studying fast reactions that have half-lives as short as a few milliseconds. In the next section, relaxation methods that can be used to study very fast reactions that have half-lives as short as 10^{-10} to 10^{-12} sec will be described.

3.8 RELAXATION TECHNIQUES

Although the vast majority of reactions used in the chemical industry to produce useful goods can be studied by conventional techniques, there are also many reactions that take place on a much shorter timescale. These include the reactions of ions in solution (such as the reaction of H_3O^+ and OH^- in neutralization) and electron transfer reactions. Classical techniques generally rely on mixing of reactants and can be used for studying reactions that take place on a timescale of approximately a few seconds or longer. Flow techniques (described in Section 3.7) reduce the timescale to perhaps

10^{-3} sec. In contrast, extremely fast reactions in solution may take place on a timescale as short as 10^{-10} to 10^{-12} sec. A time of this magnitude corresponds to the time necessary for diffusion to occur over a distance that represents the distance separating them at closest approach. That distance is typically on the order of 10^{-4} to 10^{-5} cm so the time necessary for diffusion to occur is approximately 10^{-10} to 10^{-12} sec. If long-range diffusion is involved, the reaction rate will be dependent of the viscosity of the solvent.

Relaxation techniques are designed so that mixing rates and times do not control the reaction. Instead, they utilize systems that are at equilibrium under the conditions of temperature and pressure that describe the system before some virtually instantaneous stress is placed on the system. The stress should not be a significant fraction of the half-life of the reaction. After the stress disturbs the system, chemical changes occur to return the system to equilibrium. This relieving of the stress is the reason why the term *relaxation* is applied to such experiments.

Several relaxation techniques differ primarily in the type of stress applied to the system. For example, the shock tube method makes use of two chambers that are separated by a diaphragm. The reactants are on one side of the diaphragm where the pressure is much lower than on the other, which contains a gas under much higher pressure. The high-pressure gas is known as the driver gas, and when the diaphragm is ruptured, it expands rapidly into the chamber containing the reactants. This expansion generates a shock wave that results in rapid heating of the reactant gases. The reaction between the gases occurs as the system reestablishes equilibrium. Changes in concentrations of the reactants (or products) are followed by using a spectrophotometer. Shock tube techniques can be used to study gas phase reactions that occur on the timescale of 10^{-3} to about 10^{-6} sec.

Another means of producing an instantaneous stress on a system at equilibrium is by irradiating it with a burst of electromagnetic radiation. Known as *flash photolysis*, this technique is based on the fact that absorption of the radiation changes the conditions so that the system must relax to reestablish equilibrium. As it does so, the changes can be followed spectrophotometrically.

The technique known as *temperature jump* (commonly referred to *as T-jump*) involves rapidly heating the system to disturb the equilibrium. Heating is sometimes accomplished by means of electric current or microwave radiation. When a rapid change in pressure is used to disturb the system, the technique known as *pressure jump* (shortened *to P-jump*) results.

Keep in mind that a change in pressure accomplishes P-V work that is very small compared to the effects of changing the temperature for liquids (see Section 3.6). Consequently, the P-jump technique is normally used to study reactions in gaseous systems.

Kinetic analysis of a relaxing system is somewhat different than for classical reactions as will now be described. Suppose a reaction that is first-order in both A and B can be shown as

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \tag{3.47}$$

and that the reverse reaction is first-order in C. If the reaction at equilibrium is disturbed by a stress that defines $t = 0$, the system will react to relieve the stress. After some period of reaction, the concentrations of the species will have some new values such that the *changes* in concentration can be represented as

$$\Delta[A] = [A]_f - [A]_{eq} \tag{3.48}$$

$$\Delta[B] = [B]_f - [B]_{eq} \tag{3.49}$$

$$\Delta[C] = [C]_f - [C]_{eq} \tag{3.50}$$

where the changes in concentration are small compared to the initial concentrations of the species. From the stoichiometry of the reaction, we know that the change in the concentration of A is equal to that of B and negative that of C. Therefore,

$$\Delta[A] = \Delta[B] = -\Delta[C] \tag{3.51}$$

The concentration of A at any time after the reaction starts can be expressed as

$$[A] = [A]_{eq} - \Delta[C] \tag{3.52}$$

$$[B] = [B]_{eq} - \Delta[C] \tag{3.53}$$

$$[C] = [C]_{eq} + \Delta[C] \tag{3.54}$$

If we express the rate of the reaction in terms of the amount of product formed and the amount decomposing, the rate law becomes

$$\text{Rate} = \frac{d\Delta[C]}{dt} = k_1[A][B] - k_{-1}[C] \tag{3.55}$$

Substituting the results shown in Eq. (3.52) to (3.54) for [A], [B], and [C] we obtain

$$\frac{d\Delta[\mathrm{C}]}{dt} = k_1([\mathrm{A}]_{\mathrm{eq}} - \Delta[\mathrm{C}])([\mathrm{B}]_{\mathrm{eq}} - \Delta[\mathrm{C}]) - k_{-1}([\mathrm{C}]_{\mathrm{eq}} - \Delta[\mathrm{C}]) \quad (3.56)$$

Expansion of the right-hand side of this equation leads to

$$\frac{d\Delta[\mathrm{C}]}{dt} = k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} - k_{-1}[\mathrm{C}]_{\mathrm{eq}} - k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}})\Delta[\mathrm{C}] - k_{-1}\Delta[\mathrm{C}] + k_1(\Delta[\mathrm{C}])^2 \quad (3.57)$$

At equilibrium, the rates of the forward and reverse reactions are equal, so

$$k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} = k_{-1}[\mathrm{C}]_{\mathrm{eq}} \quad (3.58)$$

In a general case, the change in concentration of C will be very small compared to the actual concentration so that the term involving $(\Delta[\mathrm{C}])^2$ can be ignored. Therefore, the rate equation reduces to

$$\frac{d\Delta[\mathrm{C}]}{dt} = -(k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}) + k_{-1})\Delta[\mathrm{C}] \quad (3.59)$$

Since all of the quantities on the right-hand side are constants except for $\Delta[\mathrm{C}]$, this equation represents a process that is first-order in $\Delta[\mathrm{C}]$. If we represent the quantity multiplied by $\Delta[\mathrm{C}]$ as τ,

$$k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}) + k_{-1} = \frac{1}{\tau} \quad (3.60)$$

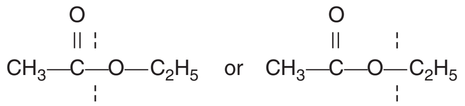
we obtain

$$\Delta[\mathrm{C}] = \Delta[\mathrm{C}]_0 e^{-\frac{t}{\tau}} \quad (3.61)$$

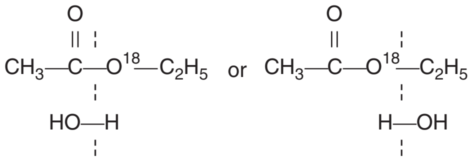
From this equation, we see that the relaxation to reestablish equilibrium follows a first-order process, and τ is known as the *relaxation time.*

3.9 TRACER METHODS

Although the methods employed in studying the kinetics of reactions can yield a great deal of important information for interpreting reaction mechanisms, some questions may still remain unanswered. For example, a kinetic study of the hydrolysis of ethyl acetate was described in Chapter 2. The reaction was found to obey a second-order rate law that is first-order in two reactants, but there is still a question to be answered: Which C–O bond breaks?



In other words, does the oxygen atom in the ester linkage show up in the acid or in the alcohol? This question can be answered only if the oxygen atom is made distinguishable from those in the bulk solvent, water. The way to do this is to study the hydrolysis of $CH_3COOC_2H_5$, which contains ^{18}O in that position. Then, hydrolysis of the ester will produce different products depending on which bond breaks. This can be illustrated as



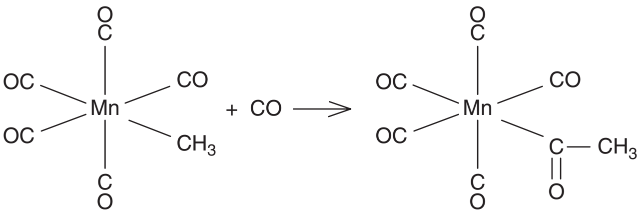
Case I, ^{18}O in alcohol Case II, ^{18}O in acid

When the hydrolysis is carried out and the products analyzed, the ^{18}O is found in the alcohol showing that Case I is correct. In some ways, this suggests that the CH_3CO^+ cation is more stable than is the $C_2H_5^+$ ion. If $C_2H_5^+$ ion were produced, it would react with the "negative group" in water (which is OH^-) and the ^{18}O would end up the alcohol.

One of the important types of reactions exhibited by coordination compounds is that known as an *insertion reaction*, in which an entering ligand is placed *between* the metal ion and a ligand already bound to it. A general form of this reaction can be shown as

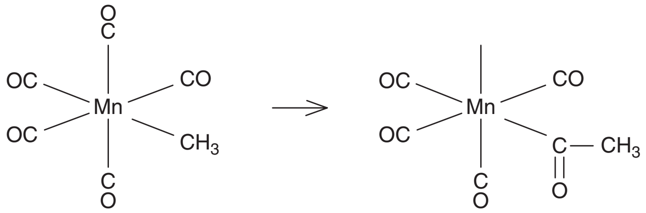
$$L_nM—X + Y \rightarrow L_nM—Y—X \qquad (3.62)$$

where M is the metal atom or ion, n is the number of ligands of type L, and X and Y are the other ligands. A well-known reaction of this type for which tracer studies have yielded important mechanistic information is the CO insertion that occurs in $[Mn(CO)_5CH_3]$. The reaction can be shown as



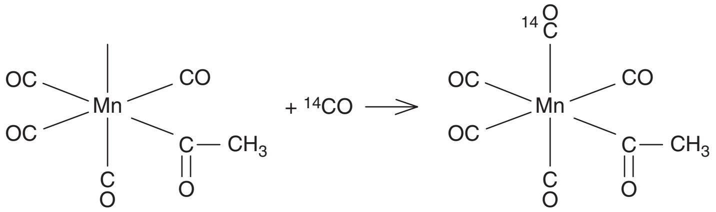
(3.63)

For this insertion reaction, it might be assumed that it is the added CO that is being inserted in the Mn—CH_3 bond. However, when the CO being added is ^{14}CO, it is found that the ^{14}C is not located in the Mn—CO—CH_3 group. The reaction actually proceeds by a first step that involves a *group transfer* of one of the CO ligands already bound to the metal. It is this ligand that is inserted between the Mn and the CH_3 group.



(3.64)

This process is followed by the addition of ^{14}CO to the metal to replace the CO molecule that has undergone migration.



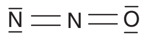
(3.65)

In this reaction, the CO that is added goes to complete the coordination sphere of the metal so it is not the one that is inserted into the Mn—CH_3 bond. Without the use of an isotopic tracer, there would be no way to distinguish one CO molecule from another.

The decomposition of NH_4NO_3 under *carefully* controlled conditions follows the equation

$$NH_4NO_3 \rightarrow N_2O + 2\ H_2O \tag{3.66}$$

Because the structure of N_2O is linear with the oxygen in a terminal position,



the nitrogen atoms are not in equivalent positions in the molecule. It would be interesting to know which nitrogen atom in N_2O came from NH_4^+ and which came from NO_3^-. In this case, using $^{15}NH_4NO_3$ and analyzing the N_2O produced (which can be done by infrared spectroscopy because the vibrations will be different depending on where the ^{15}N is located in the

molecule) shows that the product is ^{15}NNO. Therefore, the nitrate ion is not totally decomposed, and one of the oxygen atoms is found attached to the same nitrogen atom that it was initially bonded to. Although this result is not totally surprising, it is still interesting to see how tracer techniques can be used to answer questions regarding how reactions take place.

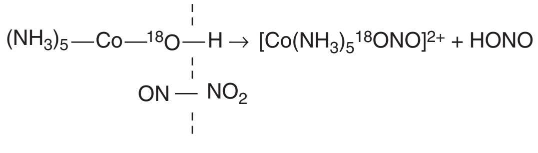
Based on the observations just described, it is possible to postulate a mechanism for the decomposition of NH_4NO_3 that is consistent with these observations. The proposed mechanism can be shown as follows.

$$NH_4^+NO_3^- \xrightarrow{-H_2O} [H_2N\text{—}NO_2] \xrightarrow{-H_2O} N = N = O \tag{3.67}$$

A reaction that appears unusual when it is first examined is

$$[Co(NH_3)_5OH]^{2+} + N_2O_3 \rightarrow [Co(NH_3)_5ONO]^{2+} + HONO \tag{3.68}$$

This reaction takes place *rapidly*, which is itself part of the unusual character because substitutions reactions of Co^{3+} low-spin complexes are usually slow. The crystal field stabilization energy in such complexes is 24Dq, and substitution reactions occur by a dissociative pathway that is normally slow. Further, the isomer produced, $[Co(NH_3)_5ONO]^{2+}$, is the *less* stable isomer with $[Co(NH_3)_5NO_2]^{2+}$ being the more stable product (see Section 3.6). It seems unlikely that the Co–OH bond would be so easily broken in this case because other Co–ligand bonds are rather inert from a kinetic standpoint. These observations led to a tracer study of this reaction, in which $[Co(NH_3)_5^{18}OH]^{2+}$ was employed. When the analysis of the products was carried out, it was found that the ^{18}O was contained in the $[Co(NH_3)_5ONO]^{2+}$ signifying that the Co–O bond is not broken during the reaction. The reaction appears to take place by a mechanism that can be shown as follows.

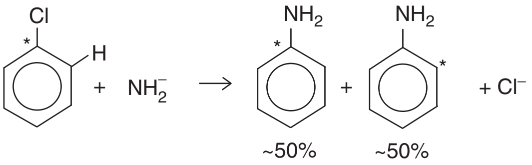


(3.69)

This process actually represents a reaction of a coordinated ligand rather than a substitution reaction. A similar result has been found for the acid hydrolysis of the carbonato complex, $[Co(NH_3)_5CO_3]^+$, which also takes place without breaking the Co–O bond.

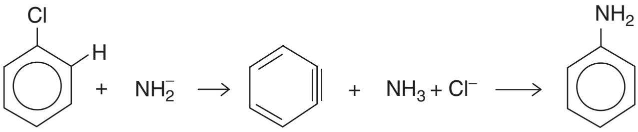
A classic example of the use of isotopically labeled compounds in organic chemistry involves the identification of the benzyne intermediate by J. D. Roberts and coworkers (1956). The reaction of chlorobenzene with

amide ion produces aniline. This reaction was studied by using ^{14}C at the 1-position (indicated by * in the following structures).



(3.70)

It is believed that the reaction takes place by the formation of the benzyne intermediate in a process that can be represented as



(3.71)

Attack by the NH_3 on the benzyne intermediate is about equally probable in forming a C–N bond at either end of the triple bond in benzyne. Therefore, the product distribution is approximately 50% of both ^{14}C—N and ^{12}C—N bonds. Employing ^{14}C in the reactant 1—^{14}C–chlorobenzene produces results that provide a way to explain which carbon atom the NH_2 group attaches to. As illustrated earlier, the use of a tracer gives information about the type of intermediate formed that is not easily obtained in any other way.

While only a few examples of the use of labeling techniques have been cited here, the reactions chosen represent drastically different types. These examples show how the use of tracers in elucidating reaction mechanisms has been of great value. In many cases, the results obtained are simply not obtainable by any other means because there is no other way to distinguish between atoms that are otherwise identical.

3.10 KINETIC ISOTOPE EFFECTS

Molecules that are chemically identical except for containing different isotopes react at different rates. For example, it is the difference in rates of electrolysis that allows D_2O to be obtained by the electrolysis of water, even though the relative abundance of D compared to H is 1:6000. This phenomenon is known as the *kinetic isotope effect.* A *primary* kinetic isotope effect occurs when isotopic substitution has been accomplished so that the

bond being broken directly involves different isotopes. A mathematical treatment of isotope effects is rather laborious and unnecessary, but we can show how they arise in a straightforward way.

It is known that the greater the *relative* difference in the mass of two isotopes, the greater the kinetic isotope effect. Therefore, the effect will be greater when H is replaced by D (where there is a 100% mass increase) than when ^{79}Br is replaced by ^{81}Br. Suitable preparation and detection procedures must be available, and a radioactive isotope must have a suitable half-life for the isotopically labeled materials to be employed. This limits somewhat the range of atoms that are useful in studying kinetic isotope effects on reaction rates. Other than studies involving isotopes of hydrogen, studies using ^{13}C or ^{14}C, ^{15}N, ^{34}S, ^{35}Cl or ^{37}Cl, and ^{79}Br or ^{81}Br are most common.

For a vibrating diatomic molecule A–B, the vibrational energy can be expressed as

$$E = \mathrm{h}\nu\left(n + \frac{1}{2}\right) \tag{3.72}$$

where h is Planck's constant, n is the vibrational quantum number, and ν is the frequency of the stretching vibration. For most diatomic molecules, the spacing between vibrational energy levels is on the order of 10 to 40 kJ/mol, and at room temperature, RT amounts to only about 2.5 kJ/mol. Therefore, practically all of the molecules will populate the lowest vibrational energy level ($n = 0$). Under these conditions or even at 0 K, the molecules will still have some vibrational energy (which is the so-called *zero-point vibrational energy*) that is given as

$$E = \frac{1}{2}\mathrm{h}\nu \tag{3.73}$$

If the vibration takes place with the molecule behaving as a harmonic oscillator, the frequency is given by

$$\nu = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2} \tag{3.74}$$

where f is the force constant for the bond and μ is the reduced mass, $m_A m_B/(m_A + m_B)$. The chemical bonds in A–B and A–B* (where B and B* are different isotopes of the same element) are very nearly identical because electronic energies are essentially unaffected by the number of neutrons in the nuclei. However, the reduced mass is affected, as we can

easily illustrate. Consider the molecules H_2, HD, and HT (where T is tritium, ^3H). For H_2, we can write the reduced mass as

$$\mu_{HH} = \frac{m_H m_H}{m_H + m_H} = \frac{m_H^2}{2m_H} = \frac{1}{2} m_H \tag{3.75}$$

Recalling that $m_D = 2m_H$, the reduced mass for HD can be written as

$$\mu_{HD} = \frac{m_H m_D}{m_H + m_D} \approx \frac{m_H(2m_H)}{m_H + 2m_H} = \frac{2}{3} m_H \tag{3.76}$$

In a similar way, we can show that $\mu_{HT} \approx (3/4)m_H$ while for D_2 the result is m_H. Only in the case of the hydrogen isotopes is the relative mass effect this large.

The effect of the reduced mass on the zero-point vibrational energy is easily seen. If we consider the molecules H–H and H–D in their lowest vibrational states, we find that the vibrational energy in terms of the force constant, *f*, can be written as

$$E = \frac{h}{4\pi}\left(\frac{f}{\mu}\right)^{1/2} \tag{3.77}$$

For the two molecules, the ratio of the zero-point energies is

$$\frac{E_{HH}}{E_{HD}} = \left(\frac{\mu_{HD}}{\mu_{HH}}\right)^{1/2} \approx \left(\frac{(2/3)m_H}{(1/2)m_H}\right)^{1/2} = (1.33)^{1/2} = 1.15 \tag{3.78}$$

This ratio of 1.15 is equal to the observed value as is shown by the zero-point vibrational energies for H–H and H–D, which are 25.9 and 22.4 kJ/mol, respectively. Similarly, it can be shown that $E_{HH}/E_{DD} = 1.41$. Since $\mu_{HD} > \mu_{HH}$, it is found that $E_{HH} > E_{HD}$ (the energy is inversely proportional to the reduces mass). As a result, the zero-point vibrational energy is *greater* for the H–H bond than it is for the H–D bond.

Because the H_2 molecule already resides in a *higher* vibrational energy state than does the HD molecule, it requires corresponding *less* energy to dissociate the H_2 molecule. Accordingly, a reaction that requires the dissociation of these molecules will take place more rapidly for H_2 than for HD.

For hydrogen or deuterium atoms bound to another atom X, which has a much larger mass, the reduced mass will be given by

$$\mu_{HX} = \frac{m_H m_X}{m_H + m_X} \approx m_H(\text{or } m_D) \tag{3.79}$$

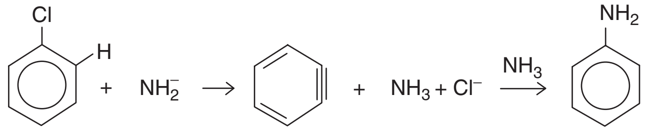
Therefore, when X has a much larger mass than H or D,

$$\frac{E_{HX}}{E_{DX}} = \left(\frac{m_D}{m_H}\right)^{1/2} = 2^{1/2} = 1.41 \qquad (3.80)$$

For O–H bonds, the absorption due to a change in vibrational energy is observed at approximately 3600 cm^{-1}, while the absorption for O–D bonds is found at approximately 2600 cm^{-1}. Similarly, the absorption band for stretching C–H bonds is normally found at $\sim$ 3000 cm^{-1}, but for D–C the band is at $\sim$ 2100 cm^{-1}. This suggests that the differences in the nature of the X–H bonds should give rise to a kinetic isotope effect when reactions occur at these bonds.

Consider two reactant molecules that are identical except that one of them contains a different isotope at the reactive site. If the bonds in the reactant molecules that link the two isotopic atoms in their positions are not broken in forming the transition state, the extent to which isotopic labeling affects the rate will be less than when those bonds are completely broken. If the formation of the transition state does not alter the bond holding the isotopic atoms, there will be no isotope effect. However, if during the formation of the transition state, the bond to the different isotopes in the reacting molecules becomes stronger, there will be an *inverse* isotope effect. This results from the fact that as the bond becomes stronger in the transition state, the heavier isotope will give a transition state having a lower zero-point vibrational energy. Because this gives an overall *lowering* of the energy of the transition state relative to the reactants, there will be a rate *increase* in the case of the heavier isotope.

Earlier in this chapter, we described the reaction of chlorobenzene with amide ion to produce aniline. The mechanism for this reaction involves the removal of H by NH_2^- to form the benzyne intermediate.



(3.81)

Because this reaction involves removal of hydrogen, the rate should be subject to a kinetic isotope effect if deuterium replaces hydrogen in the 2-position. When chlorobenzene–2d is used in the reaction, the ratio of the rate constants is found to be $k_H/k_D = 5.5$. This large kinetic isotope effect indicates that breaking of the C–H bond occurs in the rate-determining

step of the reaction. As expected, the rate of breaking the X–H bond is higher than that for breaking the X–D bond.

To this point, we have presumed that the bond breaking actually occurs as the transition state forms. Because quantum mechanically it is possible for barrier penetration to occur, tunneling must be considered as a possible reaction pathway. The transmission of a particle through a potential energy barrier is one of the basic models of quantum mechanics. We do not show the details of the solution here (see, for example, House, 2004), but it can be shown that the *transparency, T,* (also called the *transmission coefficient*) of a rectangular barrier of height U and thickness x to particles of mass M having an energy E is given by

$$T = e^{-2x\frac{8\pi^2 M}{h^2}(U - E)^{1/2}} \tag{3.82}$$

From this exponential relationship, it can be seen how the effects of several variables influence the probability of barrier penetration.

1. The transparency decreases as the height of the barrier, U, increases.
2. The transparency increases as the energy of the particles, E, increases.
3. The transparency is greater for particles of smaller mass, M.
4. The transparency decreases as the thickness of the barrier, x, increases.
5. If Planck's constant, h, were to have a value of 0, the system would no longer follow quantum mechanics (the so-called *classical limit*) and $T = 0$. That is, the particle would not pass over or through the barrier because it has an energy that is lower than the height of the barrier.

From the discussion just presented, it can be seen that particles having lower mass have a greater probability of penetrating a barrier if all other factors are equal. Likewise, the higher the energy of the particle, the higher the transmission coefficient. Both of these factors favor barrier penetration by H over that by D, so reactions that involve tunneling also show the expected kinetic isotope effect, which predicts that the lighter isotope reacts faster.

Although we have considered the separation of only diatomic molecules, the conclusions reached are still generally valid for more complex molecules. Bending vibrations are altered during a bond-breaking reaction, but because bending vibrations normally involve considerably lower energies than do stretching vibrations, they can usually be ignored in a qualitative approach to isotope effects. Therefore, breaking a bond in a polyatomic

molecule is considered to be essentially the same as that in a diatomic molecule. There may also be other effects produced by isotopic substitution at positions other than the reactive site in the molecule. These effects are usually much smaller than primary isotope effects, and they are referred to as *secondary* isotope effects. A very large number of reactions have been studied using kinetic isotope effects to obtain information about the transition states, and the information obtained has significantly increased knowledge of how reactions take place. For further details, the following references should be consulted.

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PROBLEMS

1. For $aA + bB \rightarrow$ Products, the initial rate varies with initial concentrations as follows.

$[A]_o$	$[B]_o$	R_i, $\mathbf{M}^{-1}$ sec^{-1}
0.0260	0.0320	0.000410
0.0170	0.0190	0.000159

   Use the method of initial rates and determine the overall order of the reaction.

2. For the reaction

$$3\ O_3 + Br_2O \rightarrow 3\ O_2 + 2\ BrO_2$$

   decide some aspect of the mechanism that would have different outcomes if some isotope were used. Write the question to be answered. Next, decide which atom could be replaced by a different isotope and show how the mechanism could be elucidated by the use of a labeled compound.

3. For the reaction

$$N_2H_5^+ + HNO_2 \rightarrow HN_3 + H^+ + 2\ H_2O$$

   decide some aspect of the mechanism that would have different outcomes if some isotope were used. Write the question to be answered. Next, decide which atom could be replaced by a different isotope and show how the mechanism could be elucidated by the use of a labeled compound.

4. For a reaction $aA + bB \rightarrow$ Products, the following data were obtained for the initial rates, R_i.

$[A]_o$	$[B]_o$	R_i, $\mathbf{M}^{-1}$ sec^{-1}
0.125	0.216	0.0386
0.186	0.216	0.0568
0.125	0.144	0.0176

   Use the logarithmic method to determine the rate law for the reaction.

5. For the reaction

$$[Co(NH_3)_5ONO]^{2+} \rightarrow [Co(NH_3)_5NO_2]^{2+}$$

carried out at 30°C, the rate constant varies with pressure as follows (Mares, M., Palmer, D. A., Kelm, M., *Inorg. Chim. Acta*, *1978, 27*, 153):

P, bar	10^5 *k*, sec^{-1}	P, bar	10^5 *k*, sec^{-1}
1	13.7 ± 0.3	1000	20.2 ± 0.5
250	15.9 ± 0.3	1500	21.5 ± 0.4
500	17.5 ± 0.5	2000	23.9
750	18.4 ± 0.4	2500	27.8

Use these data to determine the volume of activation for the reaction.

6. The reaction

$$2\ 2\text{−}C_5H_{10} \rightarrow 2\text{−}C_4H_8 + 3\text{−}C_6H_{12}$$

is catalyzed by $C_5H_5NMo(NO)_2Cl_2$ (Hughes, W. B., *J. Am. Chem. Soc. 1970, 92*, 532). When the catalyst concentration is 2.08×10^{-3} **M**, the rate of 2−C_5H_{10} loss is 0.73×10^2 **M** min^{-1} and when the catalyst concentration is 4.16×10^{-3} **M**, the rate is 1.30×10^2 **M** min^{-1}. Use these data and the logarithmic method to determine the order with respect to the catalyst.

CHAPTER 4

Reactions in the Gas Phase

In the previous chapters, we have considered reactions on an empirical basis in terms of several concentration-time relationships that apply to many types of chemical systems. Our intuition indicates that while the *overall* reaction may be described in this way, on a *molecular* level individual reacting ''units'' must on some microscopic scale collide or make contact in some way. These units (molecules, ions, atoms, radicals, and electrons) must be involved in some simple step at the instant of reaction. These steps through which individual units pass are called *elementary reactions*. The sequence of these elementary reactions constitutes the *mechanism* of the reaction.

In many cases, there must be energy transfer between the reacting molecules. For reactions that take place in the gas phase, molecular collisions constitute the vehicle for energy transfer, and our description of gas phase reactions begins with a kinetic theory approach to collisions of gaseous molecules. In simplest terms, the two requirements that must be met for a reaction to occur are (1) a collision must occur and (2) the molecules must possess sufficient energy to cause a reaction to occur. It will be shown that this treatment is not sufficient to explain reactions in the gas phase, but it is the starting point for the theory.

4.1 COLLISION THEORY

Normally, the rate of a reaction is expressed in terms of a rate constant multiplied by a function of concentrations of reactants. As a result, it is the rate constant that contains information related to the collision frequency, which determines the rate of a reaction in the gas phase. When the rate constant is given by the Arrhenius equation,

$$k = Ae^{-E_a/RT} \quad (4.1)$$

E_a is related to the energy barrier over which the reactants must pass as products form. For molecules that undergo collision, the exponential is related to the number of molecular collisions that have the required energy to induce reaction. The pre-exponential factor, A, is related to the frequency of collisions. Therefore, we can describe the reaction rate as

Rate = (Collision frequency) × (Fraction of collisions with at least the threshold energy)

or

$$\text{Rate} = Z_{AB} \times F \quad (4.2)$$

where Z_{AB} is the frequency of collisions between molecules of A and B and F is the fraction of those collisions having sufficient energy to cause reaction.

The collision frequency between two different types of molecules can be calculated by means of the kinetic theory of gases. In this discussion, in which collisions are occurring between molecules of A and B, we will consider the molecules of B as being stationary and A molecules moving through a collection of them. If we imagine a molecule of A moving through space where molecules of B are located, collisions will occur with molecules of B whose centers lie within a cylinder of length ν_{AB} and radius $r_A + r_B$ where ν_{AB} is the average relative velocity of A and B and $r_A + r_B$ is the sum of the radii of molecules A and B. A diagram showing this situation is shown in Figure 4.1.

We can define the cross-sectional area of the cylinder, $\pi(r_A + r_B)^2$, the *collisional cross section*, σ_{AB}. In 1 second, a molecule of A travels a distance of ν_{AB} (where ν_{AB} is the average molecular velocity of A relative to B) and it will collide with all molecules of B that have centers that lie within the cylinder. Therefore, the number of collisions per second will be given by

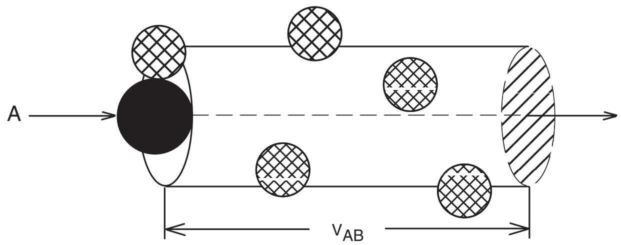

FIGURE 4.1 Model used for calculating collision frequency.

the number of B molecules/cm^3 multiplied by the volume of the cylinder. This can be expressed by the equation

$$Z_A = \nu_{AB}\sigma_{AB}C_B \tag{4.3}$$

Although A does not continue in a straight line after colliding with B, the calculated collision frequency will still be correct as long as there is no gradient in concentration of B within the container and the velocity of A remains constant. The preceding result is for a single molecule of A. To obtain the total number of collisions between molecules of A and B, Z_{AB}, the result must be multiplied by C_A, the number of molecules of A per cm^3. Therefore, the collision frequency is

$$Z_{AB} = \nu_{AB}\sigma_{AB}C_AC_B \tag{4.4}$$

Because we have considered molecules of B to be stationary (velocity = 0), the relative velocity ν_{AB} is just the root-mean-square velocity of A,

$$\nu_A = \left(\frac{8\mathbf{k}T}{m\pi}\right)^{1/2} \tag{4.5}$$

where T is the temperature (K), **k** is Boltzmann's constant, and *m* is the mass of A. Note that Boltzmann's constant is denoted in bold to distinguish it from a rate constant. If we represent the reduced mass of a pair of molecules A and B as μ, then

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \tag{4.6}$$

or, in the more familiar form,

$$\mu = \frac{m_A m_B}{m_A + m_B} \tag{4.7}$$

The relative velocity of A and B can now be written as

$$\nu_{AB} = \left(\frac{8\mathbf{k}T}{\pi\mu}\right)^{1/2} \tag{4.8}$$

Having derived an expression for the relative velocity of the molecules, the collision frequency is expressed as

$$Z_{AB} = \left(\frac{8\mathbf{k}T}{\pi\mu}\right)^{1/2} \sigma_{AB}C_AC_B \tag{4.9}$$

Frequently, the collision diameter, $d = (d_A + d_B)/2$, is used and the concentrations are written in terms of numbers of molecules/cm^3, n_A and n_B, per unit volume. Then,

$$Z_{AB} = d^2\pi\left(\frac{8\mathbf{k}T}{\pi\mu}\right)^{1/2}\frac{n_A n_B}{V^2} \tag{4.10}$$

If we consider 1 cm^3 of gaseous H_2 at 1 atm and 300 K, using a collision diameter of 0.21 nm (2.1×10^{-8}cm) we obtain a collision frequency of about 1.8×10^{29} collisions per second per cm^3. Therefore, at this collision frequency, if every collision led to a reaction, 1 mole of a gas could react in a time that is determined as

$$\frac{6.02 \times 10^{23}\ \text{molecules}}{1.8 \times 10^{29}\ \text{molecules sec}^{-1}} = 3.3 \times 10^{-6}\text{sec}$$

Since most gaseous reactions occurring between colliding molecules do not take place on this timescale, other factors than just the collision frequency must be considered. We must now consider these other factors as will now be described.

One factor that has been ignored to this point is that although a collision frequency can be calculated, the collision between the molecules must occur with sufficient energy for the reaction to occur. As we have previously seen, that minimum energy is the activation energy. Figure 4.2 shows a Maxwell-Boltzmann distribution of energies of gaseous molecules.

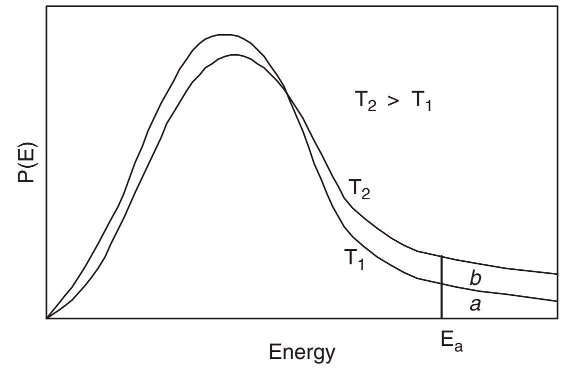

FIGURE 4.2 Distributions of molecular energies. The fraction of molecules having an energy greater than E_a is given by *a* at T_1 but it is given by *a* + *b* at T_2.

If the minimum energy to cause a reaction is the activation energy, E_a, the fraction (F) of the molecules possessing that energy or greater (represented by the areas a and b under the curve) is given by

$$F(\mathrm{E}) = \frac{\int_{E}^{\infty} \mathrm{e}^{-\mathrm{E}/\mathrm{RT}}\, d\mathrm{E}}{\mathrm{RT}} \tag{4.11}$$

When expressed in terms of the activation energy, F can be shown to be

$$F = \mathrm{e}^{-E_a/\mathrm{RT}} \tag{4.12}$$

Even if the activation energy is small, the fraction of the molecules having a collision energy leading to reaction will be a very small fraction of the total number of collisions. The reaction rate should be given by

$$\text{Rate} = \text{Collision frequency} \times \text{fraction with E} > E_a$$

$$\text{Rate} = d^2\pi\left(\frac{8\mathbf{k}\mathrm{T}}{\pi\mu}\right)^{1/2} C_A C_B \mathrm{e}^{-\mathrm{E}/\mathrm{RT}} \tag{4.13}$$

It should be noted from this equation that the collision theory of reaction rates predicts that the pre-exponential factor is not independent of temperature, but rather depends on $\mathrm{T}^{1/2}$. This occurs because the average *kinetic energy* of an ideal gas is directly proportional to T but the *average velocity* of the molecules, which determines collision frequency, is proportional to $\mathrm{T}^{1/2}$. Over a narrow range of temperature, this dependence on temperature is not usually observed. The fact is that a rather slight increase in temperature changes the average molecular velocity only very slightly because it depends on the factor $(\mathrm{T}_2/\mathrm{T}_1)^{1/2}$. However, the area under the curve corresponding to molecules having energies greater than E_a is increased slightly (see Figure 4.2). Therefore, the dominant temperature effect occurs in the $\mathrm{e}^{-E_a/\mathrm{RT}}$ factor where the fraction of molecules having $\mathrm{E} > E_a$ is calculated. As was illustrated in Chapter 2, an increase in temperature of 10° can double or triple the rate of a reaction.

When reaction rates calculated using collision theory are compared to the experimental rates, the agreement is usually poor. In some cases, the agreement is within a factor of 2 or 3, but in other cases the calculated and experimental rates differ by 10^5 to 10^7. The discrepancy is usually explained in terms of the number of *effective* collisions, which is only a fraction of the total collisions owing to steric requirements. The idea here is that in order for molecules to react, (1) collision must occur, (2) the

collision energy must be sufficient, and (3) the molecules must have a proper orientation. To compensate for the difference between calculated and observed rates, a steric factor, P, is introduced. It is defined as

$$P = \frac{\sigma_{obs}}{\sigma_{calc}} \tag{4.14}$$

This steric factor can be regarded as an orientation factor but it can also be interpreted in terms of the entropy change involved in forming the transition state.

4.2 THE POTENTIAL ENERGY SURFACE

In Chapter 1, it was shown that in one step in the reaction between H_2 and Cl_2 a chlorine radical reacts with a molecule of H_2. If we speculate about the structure of this three-body species, we realize that repulsions will be minimized if the structure is linear. Therefore, it is reasonable to assume that the elementary reaction step can be represented as shown in the sequence

$$\text{Cl}\bullet + \text{H-H} \rightarrow [\text{Cl}\cdots\text{H}\cdots\text{H}]^{\ddagger} \rightarrow \text{HCl} + \text{H}\bullet$$

and that it passes through a linear Cl···H···H transition state or activated complex. That the transition state is linear in this case follows from the fact that to form a bent transition state would bring the terminal atoms closer together, which would increase repulsion. To relate the energy of this system to the bond distances is now the problem. While we might approach this problem in a number of ways, one simple approach is to extend a relationship used for a diatomic molecule to include a second bond.

The bond energy of a diatomic molecule varies with the bond length as shown in Figure 4.3. The energy is most favorable at the bottom of the potential well which corresponds to the equilibrium bond length. One equation that models the kind of relationship shown in Figure 4.3 is the Morse equation,

$$\text{E} = \text{D}_e[e^{-2\beta(r-r_o)} - 2e^{-\beta(r-r_o)}] \tag{4.15}$$

where r is the internuclear distance, r_o is the equilibrium internuclear distance, D_e is the bond dissociation energy, and β is a constant. Attraction between the atoms increases as they get closer together (the energy becomes more negative), but at distances smaller than r_o, repulsion increases and becomes dominant at very short internuclear distances.

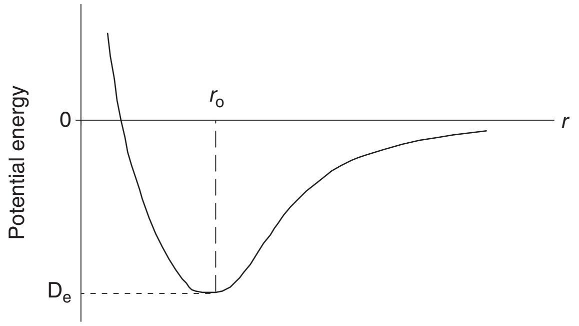

FIGURE 4.3 Potential energy curve for a diatomic molecule.

For a linear triatomic transition state, it is assumed that a second potential energy curve results so that the total energy is a function of two bond distances. Therefore, a diagram can be constructed that shows energy on one axis (usually chosen to be the vertical axis), one of the bond distances on another, and the second bond distance on the third axis, which generates a three-dimensional energy surface. If we suppose the reaction

$$AB + C \rightarrow BC + A \quad (4.16)$$

takes place with the formation of a linear transition state A···B···C, the result is a three-dimensional surface which is analogous to a contour map. In order to go from AB + C to the products BC + A it is not necessary to go over the area of highest energy (which corresponds to highly stretched bonds in the structure A···B···C). Instead, the reaction proceeds along a path where the energy rises less steeply along a "valley." Along that path, the energy barrier is lower, being similar to a pass over a mountain range between two peaks. Such a path passes over a highest point, sometimes referred to as a "saddle" point, which is lower in energy than on either side. The path representing the changes in configuration as the reaction takes place is called the *reaction coordinate*.

Since electronic energy levels for molecules differ by perhaps 200–400 kJ/mol and the motion of electrons is rapid compared to the motion of nuclei within the molecules, it is possible to determine the energy as if the nuclei were at rest (this is known as the Born-Oppenheimer approximation). The assumption is made that the coulombic and exchange energies are related by an approximately constant ratio (normally it is assumed that the exchange energy is approximately 15% of the coulombic energy). For a diatomic molecule, the energy can be written as

$$E = \frac{Q \pm J}{1 \pm S} \tag{4.17}$$

where Q, J, and S are the coulombic, exchange, and overlap integrals, respectively. For a triatomic molecule, the energy can be written as

$$E = Q_A + Q_B + Q_C \pm (1/2)\left[(J_A - J_B)^2 + (J_B - J_C)^2 + (J_A - J_C)^2\right]^{1/2} \tag{4.18}$$

where Q_A is the coulombic term for B—C, J_A is the exchange term for B—C; Q_B and J_B are the coulombic and exchange terms for A—C, and Q_C and J_C are the coulombic and exchange terms for A—B. This method, developed by London, does not reproduce known energies very accurately and it results in a shallow "basin" at the top of the saddle point. While more exact calculations based on the variation method and semi-empirical procedures provide results that are in qualitative agreement with experimental results, especially for simple molecules, the details of these methods will not be presented here. It is sufficient to point out that *ab initio* calculations have largely replaced the older type of calculations.

Another facet of the potential energy barrier to reaction is that of quantum mechanical tunneling. Classically, an object must have an energy at least equivalent to the height of a barrier in order to pass over it. Quantum mechanically, it is possible for a particle to pass *through* a barrier even though the particle has an energy that is less than the height of the barrier. In the particle in the one-dimensional box quantum mechanical model, the walls of the box are made infinitely high to prevent the particle from "leaking" from the box. The *tunneling coefficient* (also referred to as the *transmission probability* or *transparency*) of a barrier is determined by the height and thickness of the barrier and the mass and energy of the particle. For a given barrier, the transparency decreases as the mass of the particle increases so that tunneling is greater for light atoms, i.e., H, H^+, etc. However, the transparency increases as the energy approaches the barrier height (see Section 3.9).

The potential energy surface may be almost symmetrical if the diatomic molecule AB is very similar to BC. On such surfaces, the mapping of energies gives "hills" of similar energy because the bond energies are approximately equal. In a more general case, the reactant and product molecules will have considerably different bond energies so the potential energy surface will not be as nearly symmetrical. In such a case the product molecule lies at a lower energy than the reactant showing that the reaction is exothermic.

An alternative method of showing a potential energy surface is based on the same principle as that used to prepare a topographical map. In a topographical map, lines connect points of equal altitude creating contours that have specific altitudes. Where the contour lines are closely spaced, the altitude is changing abruptly, and where the contour lines are widely separated the surface is essentially flat. Slices through the surface at specific constant energies of the transition state provide the contour lines. This case corresponds to the reaction in which the molecules BC and AB have similar bond energies. For the case where BC and AB have greatly different bond energies, the surface will have one of the "valleys" as being deeper and having steeper walls, as indicated by more closely spaced contour lines.

4.3 TRANSITION STATE THEORY

A collision theory of even gas phase reactions is not totally satisfactory, and the problems with the steric factor that we described earlier make this approach more empirical and qualitative than we would like. *Transition state theory*, developed largely by Henry Eyring, takes a somewhat different approach. We have already considered the potential energy surfaces that provide a graphical energy model for chemical reactions. Transition state theory (or activated complex theory) refers to the details of how reactions become products. For a reaction like

$$AB + C \rightarrow BC + A \tag{4.19}$$

it is assumed that there is a variation in potential energy which is related to atomic coordinates by an appropriate potential energy function. The term *phase space* is applied to the coordinate and momentum space for the system. In order for a reaction to occur, the transition state must pass through some critical configuration in this space. Because of the nature of the potential function used to express the energy of the system as a function of atomic positions, the system energy possesses a saddle point. This saddle point lies lower in energy than the fully dissociated arrangement, A + B + C, or the highly "compressed" arrangement, A—B—C.

The essential feature of transition state theory is that there is a "concentration" of the species at the saddle point, the *transition state* or *activated complex*, that is in equilibrium with reactants and products. The Boltzmann Distribution Law governs the concentration of that transition state, and the rate of reaction is proportional to its concentration. Since the concentration

of the transition state is small because of its energy being higher than that of the reactants, this critical configuration represents the "regulator" of the rate of flow of reactants to products.

The concentration of the transition state is not the only factor involved, since the frequency of its dissociation into products comes into play because the rate at which it decomposes must also be considered. Therefore, the rate can be expressed as

$$\text{Rate} = (\text{Transition state concentration}) \times (\text{Decomposition frequency}) \tag{4.20}$$

In order for the transition state to separate into products, one bond (the one being broken) must acquire sufficient vibrational energy to separate. When it does separate, one of the $3N - 6$ vibrational degrees of freedom (for a linear molecule it is $3N - 5$) is lost and is transformed into translational degrees of freedom of the products. Central to the idea of transition state theory is the assumption that the transition state species is in equilibrium with the reactants. Thus,

$$\mathrm{A + B \rightleftharpoons [AB]^{\ddagger} \rightarrow \ Products} \tag{4.21}$$

For the formation of the transition state, $[\mathrm{AB}]^{\ddagger}$, the equilibrium constant is

$$\mathrm{K}^{\ddagger} = \frac{[\mathrm{AB}]^{\ddagger}}{[\mathrm{A}][\mathrm{B}]} \tag{4.22}$$

from which we find that the concentration of the transition state is

$$[\mathrm{AB}]^{\ddagger} = \mathrm{K}^{\ddagger}[\mathrm{A}][\mathrm{B}] \tag{4.23}$$

Since the reaction rate is expressed as the product of the concentration of the transition state and the frequency of its decomposition, we can now write

$$\text{Rate} = [\mathrm{AB}]^{\ddagger} \times (\text{frequency}) = (\text{frequency})\mathrm{K}^{\ddagger}[\mathrm{A}][\mathrm{B}] \tag{4.24}$$

As we have seen previously (for example, see Eq. 2.191)

$$\mathrm{K}^{\ddagger} = e^{-\Delta G^{\ddagger}/RT} \tag{4.25}$$

and we know that

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{4.26}$$

Therefore, the equilibrium constant for formation of the transition state can be written as

$$K^{\ddagger} = e^{-\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT}} = e^{-\frac{\Delta H^{\ddagger}}{RT}} \times e^{\frac{\Delta S^{\ddagger}}{R}} \quad (4.27)$$

Substituting for $K^{\ddagger}$ in Eq. (4.24) yields

$$\text{Rate} = (\text{frequency})[A][B]e^{-\frac{\Delta H^{\ddagger}}{RT}} \times e^{\frac{\Delta S^{\ddagger}}{R}} \quad (4.28)$$

Having obtained an expression for the rate in terms of concentrations and thermodynamic quantities, the frequency of decomposition of transition state must now be addressed.

If we consider the vibration of the transition state when it is at the top of the potential energy barrier, we should now recall that the classical high-temperature limit in energy for a vibrational mode can be expressed as

$$E_{vib} = \mathbf{k}T(\text{erg per molecule})$$

where **k** is Boltzmann's constant and T is the temperature (K). Since $\mathbf{k} = R/N_o$ (where N_o is Avogadro's number),

$$E_{vib} = RT(\text{Joule per mole})$$

It should also be remembered that for each degree of translational freedom the energy is $\mathbf{k}T/2$, which is $RT/2$ per mole. If we now assume that the frequency of the decomposition of the transition state is equal to the frequency of the vibration being lost due to breaking a bond as products are formed, the energy can be expressed as

$$E = h\nu = \mathbf{k}T$$

Solving for the frequency gives

$$\nu = \frac{\mathbf{k}T}{h}$$

which can also be written as

$$\nu = \frac{RT}{hN_o} \quad (4.29)$$

Because the reaction rate can be expressed in terms of the concentration of the transition state, the rate can now be given by

$$\text{Rate} = k[AB]^{\ddagger} \quad (4.30)$$

Substituting $\nu K^{\ddagger}$ for the rate constant gives

$$\text{Rate} = \nu K^{\ddagger}[A][B] \tag{4.31}$$

When we substitute the result shown in Eq. (4.29) for the frequency in this equation we obtain

$$\text{Rate} = \frac{RT}{hN_o} K^{\ddagger}[A][B] \tag{4.32}$$

The rate constant can now be written as

$$k = \frac{\mathbf{k}T}{h} K^{\ddagger} = \frac{\mathbf{k}T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}} \tag{4.33}$$

A somewhat more elegant approach to deriving an expression for the rate of passage over the potential energy barrier is based on statistical mechanics. According to this procedure, it is assumed that there is a certain distance, *d*, at the top of the barrier, which must be the distance where the transition state exists. It is within this distance that a vibrational mode of the complex is transformed into translational motion of the products. The rate of passage of the transition state through distance *d* is related to the molecular velocity in one direction. If the mass of the transition state is $m^{\ddagger}$, the average velocity is

$$\nu = \left(\frac{2\mathbf{k}T}{\pi m^{\ddagger}}\right)^{1/2} \tag{4.34}$$

Therefore, the time required for the transition state to pass through distance *d* is given by

$$\frac{d}{\nu} = d\left(\frac{m^{\ddagger}\pi}{2\mathbf{k}T}\right)^{1/2} \tag{4.35}$$

The number of complexes crossing the potential barrier through distance *d* per unit time is

$$\frac{d[\ddagger]}{dt} = \frac{\dfrac{[\ddagger]}{2}}{d\left(\dfrac{\pi m^{\ddagger}}{2\mathbf{k}T}\right)^{1/2}} = \frac{[\ddagger]}{d}\left(\frac{\mathbf{k}T}{2\pi m^{\ddagger}}\right)^{1/2} \tag{4.36}$$

Note that we are using $[\,]^{\ddagger}$ to represent the transition state and $[\ddagger]$ to represent the *concentration* of the transition state. Now, the concentration

of the transition state, [‡], is to be evaluated. If the difference between the zero-point energies of the reactants and the transition state is represented as $E_o^{\ddagger}$, the equilibrium constant for formation of the transition state is given by

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q_A Q_B} e^{-\frac{E_o^{\ddagger}}{RT}} \tag{4.37}$$

where Q_A, Q_B, and $Q^{\ddagger}$ are the partition functions of reactants A and B and the transition state, respectively. If the vibrational mode of the transition state is factored out of Q we can write

$$Q^{\ddagger} = Q^{\ddagger\prime} \times q_v^{\ddagger} \tag{4.38}$$

where $q_v^{\ddagger}$ is the vibrational mode of the bond being broken. Now we can approximate the vibrational mode as

$$q_v^{\ddagger} = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} = \frac{\mathbf{k}T}{h\nu^{\ddagger}} \tag{4.39}$$

and the equilibrium constant $K^{\ddagger}$ is given by

$$K^{\ddagger} = \frac{\mathbf{k}T}{h\nu^{\ddagger}} \frac{Q^{\ddagger\prime}}{Q_A Q_B} e^{-\frac{E_o^{\ddagger}}{RT}} \tag{4.40}$$

which is of the same form found earlier with the rate constant, *k*, being given by

$$k = \frac{\mathbf{k}T}{h} \frac{Q^{\ddagger\prime}}{Q_A Q_B} e^{-\frac{E_o^{\ddagger}}{RT}} \tag{4.41}$$

The resemblance of this equation to the Arrhenius equation is apparent when the pre-exponential factor includes the frequency factor and the equilibrium constant in terms of partition functions. This expression for *k* is similar to that obtained from collision theory.

An approximate rate constant, k_a, can be calculated from probability that the reactants in the distribution of quantum state will collide and react in accord with the collision frequency. The approximate constant is greater than the measured rate constant, *k*. One approach to improving transition state theory with respect to calculating the rate constant is to alter the configuration of the transition state used in the energy calculations in order to effect a change in k_a. In fact, the calculations are performed in such a way that the calculated rate constant is a minimum and thereby approaches the observed *k*. Just as energy minimization is accomplished by means of the

variation method in quantum mechanical calculations, this procedure is referred to in this connection as *variational transition state theory.*

Because the free energy of activation is given by

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{4.42}$$

this procedure amounts to configuration optimization to minimize $K^{\ddagger}$ or maximize $\Delta G^{\ddagger}$. In practice, a series of transition states is considered and the calculations are performed to obtain the desired minimization. It is of some consequence to choose the reaction path with respect to the energy surface. Generally, the path chosen is the path of steepest descent on either side of the saddle point. This path represents the path of minimum energy. While the details will not be presented here, the rate constant can now be treated as a function of a coordinate related parameter, z, so that

$$k(z)^{VT} = \frac{\mathbf{k}T}{h}\frac{Q^{VT}}{Q_A Q_B} e^{-\frac{E(z)}{RT}} \tag{4.43}$$

The parameter z is related to the path (chosen as a function of coordinates) of the transition state. This expression can also be written as

$$k(z)^{VT} = \frac{\mathbf{k}T}{h} K^{\ddagger} e^{-\frac{\Delta G^{\ddagger}(z)}{RT}} \tag{4.44}$$

The value of $k(z)^{VT}$ can now be minimized with respect to z. Accordingly, the rate constant is minimized with respect to a parameter related to configuration of the transition state in the same way that energy is minimized with respect of variables in a trial wave function. Although this topic will not be described further here, details have been published in several places (for example, see Truhlar, 1980).

4.4 UNIMOLECULAR DECOMPOSITION OF GASES

The collision theory of gaseous reactions requires two molecules to collide, suggesting that such reactions should be second-order. Many decompositions, e.g., N_2O_5, appear to be first-order at sufficiently high pressures of the gas. However, some such reactions do appear to be second-order at low gas pressure. In 1922, Lindemann proposed an explanation of these observations.

Molecules transfer energy as a result of molecular collisions. Therefore, translational energy can be transferred to one molecule by another thereby

raising the translational and vibrational energy of the second molecule. The activation of molecules by collision can thus be accomplished. However, the activated molecule need not react immediately, and, in fact, it may become deactivated by undergoing subsequent collisions before it reacts. For reaction to occur, the activated molecule that has increased vibrational energy must have some bond activated to the point where bond rupture occurs.

The elementary reactions by which A is converted into products can be shown as

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + A^* \tag{4.45}$$

$$A^* \xrightarrow{k_2} \text{Products} \tag{4.46}$$

In this scheme, A^* is the activated molecule of A. Although the process producing A^* is bimolecular, the decomposition of A^* is unimolecular. The change in [A] with time can be expressed by the equation

$$-\frac{d[A]}{dt} = k_1[A]^2 - k_{-1}[A][A^*] \tag{4.47}$$

Since A^* is an activated molecule, a reactive intermediate, the steady state approximation is assumed to apply (see Section 2.4). The rate of formation of A^* is assumed to be equal to its rate of decomposition. Therefore,

$$\frac{d[A]}{dt} = 0 = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*] \tag{4.48}$$

The first term on the right-hand side of the equation represents the rate of activation of A while the second and third terms represent deactivation and decomposition of A^*, respectively. Solving Eq. (4.48) for $[A^*]$, we obtain

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \tag{4.49}$$

Substituting this result in Eq. (4.47), we obtain

$$-\frac{d[A]}{dt} = \frac{k_1 k_2[A]^2}{k_{-1}[A] + k_2} \tag{4.50}$$

At high pressures, the number of A molecules per unit volume is large, and deactivation of A^* can occur by frequent collisions with other molecules of A. Under these conditions, we will consider the rate of deactivation

of A^* to be large compared to the rate of decomposition. Therefore, $k_{-1}[A] >> k_2$ and

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \approx \frac{k_1 k_2 [A]^2}{k_{-1}[A]} = k[A] \tag{4.51}$$

where $k = k_1 k_2 / k_{-1}$. Therefore, at relatively high pressure where [A] is high, the reaction appears to be unimolecular (first-order) in [A].

At low pressures of A, the rate of decomposition of A^* is greater than the rate of its deactivation by collision with A because there are fewer molecules of A available. Under these conditions, the increase in vibrational energy can cause bond rupture and decomposition. Therefore, in this case, $k_2 >> k_{-1}[A]$ and

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_2} = k_1[A]^2 \tag{4.52}$$

This equation shows that at low pressures of the reacting gas, the reaction should be bimolecular (second-order). Thus, the observed bimolecular dependence at low pressure and the unimolecular dependence at high pressure are predicted by a mechanism involving activation of molecules by collision.

The activation of reactant molecules by collision was described earlier. However, this is not the only vehicle for molecular activation. It is possible for a non-reactant gas (a so-called third body) to cause activation of molecules of the reactant. If we represent such a species by M, the processes of activation, deactivation, and product production are given by

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M \tag{4.53}$$

$$A^* \xrightarrow{k_2} \text{Products} \tag{4.54}$$

Therefore, the rate of disappearance of A can be written as

$$-\frac{d[A]}{dt} = k_1[A][M] - k_{-1}[A^*][M] \tag{4.55}$$

The net change in concentration of A^* with time is given by the difference between the rate at which it is formed as represented in Eq. (4.53) and the rate at which it is removed by undergoing reaction as shown in Eq. (4.54).

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k^2[A^*] = 0 \tag{4.56}$$

Therefore, rearrangement gives

$$0 = k_1[\mathrm{A}][\mathrm{M}] - (k_{-1}[\mathrm{M}] + k_2)[\mathrm{A}^*] \tag{4.57}$$

and solving for $[\mathrm{A}^*]$ yields

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} \tag{4.58}$$

Substituting for $[\mathrm{A}^*]$ in Eq. (4.55) gives

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}[\mathrm{M}]\frac{k_1[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} \tag{4.59}$$

Factoring out the quantity $k_1[\mathrm{A}][\mathrm{M}]$ on the right-hand side enables us to write this equation in the form

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}]\left(1 - \frac{k_{-1}[\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}\right) \tag{4.60}$$

The quantity inside the parentheses can be made into a single fraction to give

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}]\left(\frac{k_{-1}[\mathrm{M}] + k_2}{k_{-1}[\mathrm{M}] + k_2} - \frac{k_{-1}[\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}\right) \tag{4.61}$$

This equation can now be written as

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}]\left(\frac{k_{-1}[\mathrm{M}] + k_2 - k_{-1}[\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}\right) \tag{4.62}$$

and simplified to obtain

$$-\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2[\mathrm{M}][\mathrm{A}]}{k_{-1}[\mathrm{M}] + k_2} \tag{4.63}$$

The results obtained by considering activation by a third body must now be compared to those described earlier for activation by collision of reactant molecules.

At high pressure, the rate of deactivation by collisions with M is likely to be greater than the rate of reaction, so $k_{-1}[\mathrm{M}] >> k_2$ and neglecting k_2 in the denominator of Eq. (4.63) gives

$$-\frac{d[\mathrm{A}]}{dt} \approx \frac{k_1 k_2[\mathrm{M}][\mathrm{A}]}{k_{-1}[\mathrm{M}]} \approx k'[\mathrm{A}] \tag{4.64}$$

This approximation shows that the reaction follows a first-order rate law. At low pressure, the concentration of M is low, so $k_{-1}[M] << k_2$ and

$$-\frac{d[A]}{dt} \approx \frac{k_1 k_2[M][A]}{k_2} \approx k_1[A][M] \tag{4.65}$$

Therefore, the reaction appears to be first-order in A and first-order in M. If the species M is simply another molecule of reactant A, this equation becomes

$$-\frac{d[A]}{dt} = k_1[A]^2 \tag{4.66}$$

which is the second-order rate expression found earlier. These results are in accord with experience for the unimolecular decomposition of a large number of gaseous compounds.

Ozone decomposes by a mechanism that appears to be somewhat different from that described earlier, but it provides a rather simple application of the steady state approximation. The overall reaction is

$$2O_3(g) \rightarrow 3O_2(g) \tag{4.67}$$

for which the observed rate law is

$$-\frac{d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]} \tag{4.68}$$

Therefore, the reaction is second-order in ozone but the reaction is inhibited by O_2. This reaction is believed to involve a third body (an inert molecule or particle) in the steps

$$O_3(g) + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) + M \text{ (fast)} \tag{4.69}$$

$$O(g) + O_3(g) \xrightarrow{k_2} 2O_2(g) \text{ (slow)} \tag{4.70}$$

The rate constant for the second reaction is much smaller than that for the first, so the second reaction is rate determining. Therefore, the rate equation is written as

$$-\frac{d[O_3]}{dt} = k_2[O][O_3] \tag{4.71}$$

The rate of O formation is given by

$$\frac{d[O]}{dt} = k_1[M][O_3] \tag{4.72}$$

and the rate of consumption of O is

$$-\frac{d[O]}{dt} = k_{-1}[M][O][O_2] \tag{4.73}$$

Therefore, applying the steady state approximation,

$$k_1[M][O_3] = k_{-1}[M][O][O_2] \tag{4.74}$$

Solving this equation for [O] we obtain

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]} \tag{4.75}$$

which when substituted in Eq. (4.71) gives

$$-\frac{d[O_3]}{dt} = k_2[O_3] \cdot \frac{k_1[O_3]}{k_{-1}[O_2]} = k\frac{[O_3]^2}{[O_2]} \tag{4.76}$$

This is the form of the observed rate law where $k = k_1k_2/k_{-1}$.

The approach of Lindemann is based on collisional activation of molecules as a result of energy transfer. C. N. Hinshelwood (Nobel Prize in 1956) extended this approach to include changes in vibrational energies that can be distributed internally to supply sufficient energy to the bond being broken. This approach provided a better fit to observed kinetics in the region of low pressure.

In the late 1920s, O. K. Rice and H. C. Ramsperger as well as L. S. Kassel developed an approach (now known as the RRK theory) to unimolecular decomposition reactions which is based on statistically treating the molecules as coupled oscillators. In this way, energy is presumed to be distributed about the energized molecule until it vibrates in a way that results in bond rupture. In this treatment, it is assumed that the amount of energy, E^*, must be localized in the bond being broken and that the probability of this happening is given by

$$P = \left(\frac{E - E^*}{E}\right)^{N-1} \tag{4.77}$$

where N is the number of vibrational modes ($3N - 5$ for linear molecules and $3N - 6$ for nonlinear molecules). The rate constant is presumed proportional to the probability, so it is given by

$$k = \left(\frac{E - E^*}{E}\right)^{N-1} \tag{4.78}$$

It can then be shown that at high pressure

$$k = e^{-E^*/\mathbf{k}T} \tag{4.79}$$

A later modification of the RRK theory presented by R. A. Marcus (*J. Chem. Phys.*, 1952, *20*, 359) (Nobel Prize in 1992) resulted in the so-called RRKM theory. In this case, the mechanism of the reaction consists of the following steps

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M \tag{4.80}$$

$$A^* \xrightarrow{k_2} A^{\ddagger} \tag{4.81}$$

$$A^{\ddagger} \xrightarrow{k_3} \text{Products} \tag{4.82}$$

The essential idea is that the activated *molecule*, A^*, becomes the *transition state* or *activated complex*, $A^{\ddagger}$, which then leads to product formation. This is presumed to occur when the energy at the reactive site becomes as large as E_a, the activation energy. The rate at which A^* is transformed into A depends on the number of degrees of vibrational freedom. Therefore, the theory is concerned with the treatment of the vibrational frequencies of A^* and A in the calculations.

From the preceding processes, we can write the rate law

$$-\frac{d[A]}{dt} = k_1[A][M] - k_{-1}[A^*][M] \tag{4.83}$$

Applying the steady state approximation with regard to A^* gives

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0 \tag{4.84}$$

Therefore, the concentration of A^* can be expressed as

$$[A^*] = \frac{k_1[A][M]}{k_2 + k_{-1}[M]} \tag{4.85}$$

From Eq. (4.84), we find that

$$k_{-1}[A^*][M] = k_1[A][M] - k_2[A^*] \tag{4.86}$$

Therefore, substituting for $k_{-1}[A^*][M]$ in Eq. (4.83) yields

$$-\frac{d[A]}{dt} = k_1[A][M] - k_{-1}[A^*][M] = k_1[A][M] - (k_1[A][M] - k_2[A^*]) \tag{4.87}$$

which can be simplified to obtain

$$-\frac{d[A]}{dt} = k_2[A^*] \tag{4.88}$$

Now, substituting the expression shown in Eq. (4.85) for $[A^*]$ gives

$$-\frac{d[A]}{dt} = \frac{k_1 k_2[A][M]}{k_2 + k_{-1}[M]} = \left(\frac{k_1 k_2[M]}{k_2 + k_{-1}[M]}\right)[A] \tag{4.89}$$

We can now consider the quantity in brackets as the rate constant for the formation of product or disappearance of A. If $k_{-1}[M] >> k_2$, the equation reduces to

$$-\frac{d[A]}{dt} = k'[A] \tag{4.90}$$

where $k' = k_1 k_2 / k_{-1}$ and the reaction appears to be first-order in A. If $k_2 >> k_{-1}[M]$, the rate shown in Eq. (4.89) becomes

$$-\frac{d[A]}{dt} = k_1[A][M] \tag{4.91}$$

and, when the third body, M, is a second molecule of A, the equation becomes

$$-\frac{d[A]}{dt} = k_1[A]^2 \tag{4.92}$$

Therefore, the reaction shows a second-order dependence on A. Many of the details of the Marcus theory can be found in the book by Nicholas (1976).

4.5 FREE RADICAL OR CHAIN MECHANISMS

Some of the elementary concepts of free radical mechanisms were presented in Chapter 1. Reactions following free radical mechanisms have reactive intermediates containing unpaired electrons which are produced by homolytic cleavage of covalent bonds. A method of detecting free radicals was published in 1929, and it is based on the fact that metals such as lead react with free radicals. When heated, tetramethyl lead decomposes,

$$(CH_3)_4Pb \rightarrow Pb + 4\ CH_3\bullet \tag{4.93}$$

A lead mirror is produced in a heated glass tube when tetramethyl lead is passed through it. Also, the lead mirror in a cool portion of the tube can be

removed by passing tetramethyl lead through a hot potion of the tube first to produce $CH_3\bullet$ radicals. In the cool portion of the tube, the reaction is

$$4\ CH_3\bullet + Pb \rightarrow (CH_3)_4Pb \tag{4.94}$$

However, if the flow system is arranged so that a long tube is used and considerable distance separates the point where the $CH_3\bullet$ radicals are generated and they react with the cool lead mirror, the reaction is hindered because of radical recombination.

$$2\ CH_3\bullet \rightarrow C_2H_6 \tag{4.95}$$

Perhaps the best known example of a chain process, certainly it is the classic case, is the reaction

$$H_2 + Br_2 \rightarrow 2\ HBr \tag{4.96}$$

This reaction was studied by Bodenstein and Lind nearly 90 years ago, and the rate law found was written as

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'\left(\frac{[HBr]}{[Br_2]}\right)} \tag{4.97}$$

where k and k' are constants with $k' = 10$. The [HBr] in the denominator indicates that the rate is decreased as [HBr] increases so that HBr functions as an inhibitor. The reaction has now been studied both thermally and photochemically and the initiation step is now agreed to be

$$Br_2 \rightarrow 2\ Br\bullet \tag{4.98}$$

The overall reaction scheme was postulated in 1919 by Christiansen, Herzfeld, and Polyani in three separate publications.

The overall process is now described in terms of the elementary steps

$$Br_2 \xrightarrow{k_1} 2\ Br\bullet \tag{4.99}$$

$$Br\bullet + H_2 \xrightarrow{k_2} HBr + H\bullet \tag{4.100}$$

$$H\bullet + Br_2 \xrightarrow{k_3} HBr + Br\bullet \tag{4.101}$$

$$H\bullet + HBr \xrightarrow{k_4} H_2 + Br\bullet \tag{4.102}$$

$$2\ Br\bullet \xrightarrow{k_5} Br_2 \tag{4.103}$$

Simplification of the mathematical problem is achieved by application of the steady state hypothesis to those species that occur only in the propagation steps. In this case, it is assumed that [Br•] and [H•] are at some low, essentially constant level. Therefore,

$$\frac{d[\mathrm{Br}\bullet]}{dt} = 0 \text{ and } \frac{d[\mathrm{H}\bullet]}{dt} = 0 \tag{4.104}$$

Following the same type of treatment as was used in cases described in Chapter 2, we express [Br•] and [H•] in terms of their rates of formation and disappearance. Therefore, for simplicity using [H] and [Br] instead of [H•] and [Br•], we can write the equation giving the change in concentration of H with time from the preceding elementary steps as

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] = 0 \tag{4.105}$$

The equation giving the change in concentration of Br with time can be written as

$$\frac{d[\mathrm{Br}]}{dt} = 2k_1[\mathrm{Br_2}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{H}][\mathrm{HBr}] - 2k_5[\mathrm{Br}]^2 = 0 \tag{4.106}$$

Now we can also write the equation that gives the production of HBr as

$$\frac{d[\mathrm{HBr}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] \tag{4.107}$$

If we subtract Eq. (4.105) from Eq. (4.107), while letting $d[\mathrm{H}]/dt = 0$,we obtain

$$\begin{aligned}\frac{d[\mathrm{HBr}]}{dt} - 0 = {} & k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] \\ & - \{k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}]\}\end{aligned} \tag{4.108}$$

Simplification of this equation leads to

$$\frac{d[\mathrm{HBr}]}{dt} = 2k_3[\mathrm{H}][\mathrm{Br_2}] \tag{4.109}$$

Adding Equations (4.105) and (4.106) gives

$$\begin{aligned}0 = {} & k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}]\,]\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] + 2k_1[\mathrm{Br_2}] \\ & - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{H}][\mathrm{HBr}] - 2k_5[\mathrm{Br}]^2\end{aligned} \tag{4.110}$$

which can be simplified to give

$$2k_1[Br_2] - 2k_5[Br]^2 = 0 \tag{4.111}$$

Solving this equation for [Br] yields

$$[Br] = \{(k_1/k_5)[Br_2]\}^{1/2} \tag{4.112}$$

Substitution of this value for [Br] in Eq. (4.105) gives

$$k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = k_2\{(k_1/k_5)[Br_2]\}^{1/2}[H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0 \tag{4.113}$$

$$k_2\{(k_1/k_5)[Br_2]\}^{1/2}[H_2] - [H](k_3[Br_2] - k_4[HBr]) = 0 \tag{4.114}$$

Solving this equation for [H] yields

$$[H] = \frac{k_2\left(\dfrac{k_1}{k_5}[Br_2]\right)^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \tag{4.115}$$

Substituting this result for [H] in Eq. (4.109) we obtain

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2] = \frac{2k_2k_3\left(\dfrac{k_1}{k_5}[Br_2]\right)^{1/2}[H_2][Br_2]}{k_3[Br_2] + k_4[HBr]} \tag{4.116}$$

This equation can be simplified to obtain

$$\frac{d[HBr]}{dt} = \frac{2k_2k_3\left(\dfrac{k_1}{k_5}\right)^{1/2}[H_2][Br_2]^{3/2}}{k_3[Br_2] + k_4[HBr]} \tag{4.117}$$

Dividing numerator and denominator of the right-hand side of this equation by $k_3[Br_2]$ gives

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\dfrac{k_1}{k_5}\right)^{1/2}[H_2][Br_2]^{1/2}}{1 + \dfrac{k_4[HBr]}{k_3[Br_2]}} \tag{4.118}$$

If we let $k = 2k_2(k_1/k_5)^{1/2}$ and $k' = k_4/k_3$, Eq. (4.118) has the same form as the empirical rate law shown in Eq. (4.97). We need now to examine the relationships between the rate constants. The bond energies for the molecular species in Steps 3 and 4 (Eqs. (4.101) and (4.102)) are as follows:

H—H, 436; Br—Br, 193; and H—Br, 366 kJ/mol. Therefore, both Steps 3 and 4 are exothermic having enthalpies of about −173 and −70 kJ/mol, respectively. Activation energies for forming the transition states [H···Br···Br] and [H···H···Br] are very low so there will be almost no temperature dependence on the rates of their formation and the temperature effects will approximately cancel. Therefore, the ratio k_4/k_3 is constant, having a value of 10.

Other reactions in the chain process could conceivably include

$$H_2 \rightarrow 2\ H\bullet \tag{4.119}$$

but the bond energy for H_2 is about 436 kJ/mol while that for Br_2 is 193 kJ/mol. Consequently, any dissociation involving H_2 would be insignificant compared to the dissociation of Br_2. Likewise, the dissociation of HBr to give H• and Br• would be energetically unfavorable as would the reaction

$$Br\bullet + HBr \rightarrow H\bullet + Br_2 \tag{4.120}$$

Finally, the reactions

$$H\bullet + H\bullet \rightarrow H_2 \tag{4.121}$$

$$H\bullet + Br\bullet \rightarrow HBr \tag{4.122}$$

can be considered as unlikely at best owing to the very low stationary state concentrations of these H• radicals. There are other arguments against these processes as well.

Radicals are generated, consumed, or propagated by a relatively few types of elementary reactions. Radical generation usually involves the homolytic dissociation of some covalent bond.

$$—X - Y— \rightarrow —X\bullet + —Y\bullet \tag{4.123}$$

In this case, the process is a high-energy one so it is usually brought about by thermal, photochemical, or electrical means. The consumption of radicals occurs in termination steps, which include processes like

$$Br\bullet + Br\bullet \rightarrow Br_2 \tag{4.124}$$

$$\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6 \tag{4.125}$$

The propagation of radicals can involve a transfer of atoms, which can be shown as

$$XY + Z\bullet \rightarrow XZ + Y\bullet \tag{4.126}$$

The reaction

$$H\bullet + Br_2 \rightarrow HBr + Br\bullet \quad (4.127)$$

is a previously seen example. In other cases, a radical may add to another molecule to produce a different radical.

$$XY + Z\bullet \rightarrow XYZ\bullet \quad (4.128)$$

An example of this type of process is

$$H\bullet + C_2H_4 \rightarrow C_2H_5\bullet \quad (4.129)$$

All of these processes as well as numerous examples of each type are discussed more fully by Nicholas (1976).

A further complication of chain mechanisms is the process known as *branching*. In this case, one radical results in more than a single radical being produced so the number of radicals present is increasing as the reaction proceeds. This results in an autocatalytic reaction that may, as in the reaction of H_2 and O_2, lead to an explosion under certain conditions. The reaction of H_2 and O_2 is a very complicated process that depends on the pressure of the gases, the temperature, and the type of reaction vessel. Some of the reactions involved under certain conditions are believed to be the following, although other steps may also be involved.

$$H_2 + O_2 \xrightarrow{\text{wall}} 2\ OH\bullet \qquad \text{Initiation} \quad (4.130)$$

$$\bullet OH + H_2 \rightarrow H_2O + H\bullet \qquad \text{Propagation} \quad (4.131)$$

$$H\bullet + O_2 + M \rightarrow HO_2\bullet + M \qquad \text{Propagation} \quad (4.132)$$

$$H\bullet + O_2 \rightarrow OH\bullet + \bullet O\bullet \qquad \text{Branching} \quad (4.133)$$

$$\bullet O\bullet + H_2 \rightarrow OH\bullet + H\bullet \qquad \text{Branching} \quad (4.134)$$

$$H\bullet \xrightarrow{\text{wall}} H_2 \qquad \text{Termination} \quad (4.135)$$

The overall mechanism is quite complex, and the reader is refered to other sources dealing with gas phase reactions for details (Nicholas, 1976).

4.6 ADSORPTION OF GASES ON SOLIDS

A large number of reactions, many of them of great technological importance, involve the reaction of gases on solid surfaces. The reactions

$$N_2 + 3\ H_2 \xrightarrow{\text{Fe, oxides}} 2\ NH_3 \quad (4.136)$$

$$4\ NH_3 + 5\ O_2 \xrightarrow{Pt} 4\ NO + 6\ H_2O \tag{4.137}$$

$$RCH = CH_2 + H_2 \xrightarrow{\text{Ni, Pd, or Pt}} RCH_2CH_3 \tag{4.138}$$

$$CO + \text{hydrocarbons} + O_2 \xrightarrow{CuO,\ Cr_2O_3} CO_2 + H_2O \tag{4.139}$$

are but a few examples of such cases. Although it is appropriate to consider such interfacial processes in terms of the nature of the solids, the fact that the reactants are gases makes it logical to include this topic as part of the treatment of reactions in the gas phase. When a solid catalyzes a reaction, the gaseous reactants are attached in some way before the reaction takes place. *Heterogeneous catalysis* is a process in which a solid has gaseous reactants attached that subsequently react. Consequently, it is necessary to begin a discussion of heterogeneous catalysis by describing the process of adsorption in some detail.

In the interior of a solid lattice, each unit (atom, molecule, or ion) is surrounded by others on all sides. On the surface, the units are not surrounded on one side and, therefore, they can form bonds to other species. While this process may take place by adsorption of molecules or ions from solutions, we are more concerned here with adsorption of gaseous molecules. It is also possible for gaseous reactants to penetrate below the surface of the solid in some cases. The sites on the solid where the gases are adsorbed are called *active sites*. The solid material doing the adsorbing is called the *adsorbent* and the substance adsorbed is called the *adsorbate*.

Interactions between adsorbates and adsorbents cover a wide range of energies. On the one hand, the interactions may be the result of weak van der Waals forces, while on the other, the bonds may represent strong chemical bonding of the adsorbate to the adsorbent. The distinction is not always a clear one, but physical adsorption (*physisorption*) is generally associated with heats of adsorption of 10–25 kJ/mol, while chemical adsorption (*chemisorption*) is associated with heats of adsorption of 50–100 kJ/mol. In either case, there is presumed to be a relationship between energy and the relative adsorbent/adsorbate position on the surface similar to that shown in Figure 4.4.

In general, it is believed that in cases of physical adsorption the bonding to the surface is so weak that the adsorbent molecules are changed only very slightly by the adsorption process. Therefore, physical adsorption does not weaken the bonds in the adsorbate molecules significantly, and the adsorbent does not function as a catalyst.

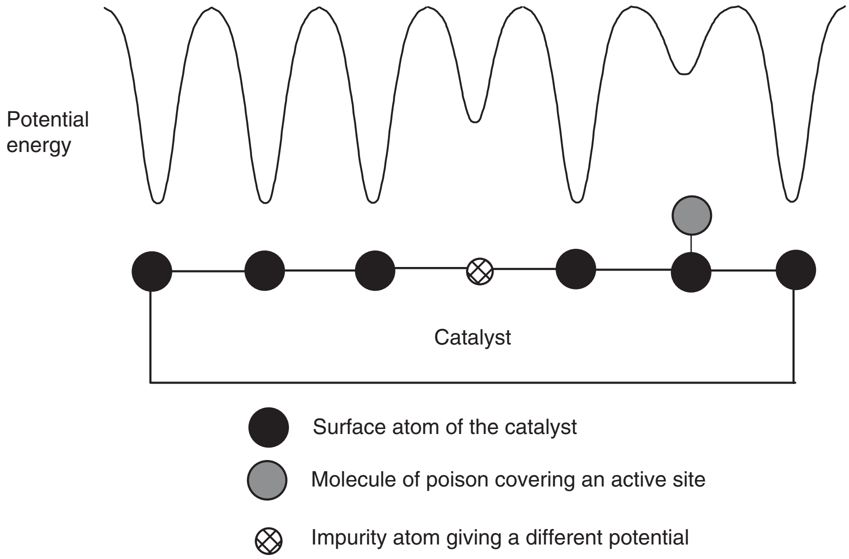

FIGURE 4.4 Variation in potential energy near the surface of a solid catalyst.

On an atomic scale, adsorption can be considered by quantum mechanical techniques. In this treatment, it is assumed that the forces between the adsorbate and the adsorbent are essentially chemical in nature. In that case, the interaction energy is calculated using techniques that are the standard ones in molecular quantum mechanics. However, the energy of a molecule being adsorbed on the surface of a solid is related to distance from the adsorbing site in such a way that the relationship results in a potential energy curve similar to the Morse potential for a diatomic molecule (see Figure 4.3). Calculations should produce curves of similar shape, and the calculated energies should match the measured energies. This is a rather formidable task and the results are not always good. Significant progress has been made in this area using extended Hückel molecular orbital (EHMO), self-consistent field (SCF), and complete neglect of differential overlap (CNDO) approaches. A brief review of these results has been given by White (1990). We will now turn our attention to describing the process of adsorption from a bulk macroscopic point of view.

4.6.1 Langmuir Adsorption Isotherm

For chemisorption, one of the most successful approaches for describing the quantitative relationships is that developed by Irving Langmuir. In this

approach, it is assumed that the adsorption process is taking place isothermally and that the uniform adsorbent surface can be covered with a monolayer of adsorbate. Further, it is assumed that there is no interaction between adsorbed molecules and that the available sites all have the same affinity for the gaseous adsorbent.

If the area of the adsorbent is represented as A and the fraction of the surface that is covered by adsorbate is f, we can derive the relationship for adsorption as follows. For an equilibrium involving adsorption, we can let the rate of condensation be equal to the rate of evaporation. The rate of evaporation will be proportional to f, the fraction of the surface covered, while the rate of condensation will be proportional to $(1-f)$, the fraction of the surface which is uncovered, and the pressure of the gas. Therefore, when these rates are equal, we can write

$$k_c(1-f)P = k_e f \tag{4.140}$$

If this equation is solved for f, we obtain

$$f = \frac{k_c P}{k_e + k_c P} \tag{4.141}$$

where P is the pressure of the gas. Dividing both the numerator and denominator of the right-hand side of Eq. (4.141) by k_e and letting $K = k_c/k_e$ gives

$$f = \frac{KP}{1 + KP} \tag{4.142}$$

This relationship, known as the *Langmuir isotherm*, is shown graphically in Figure 4.5.

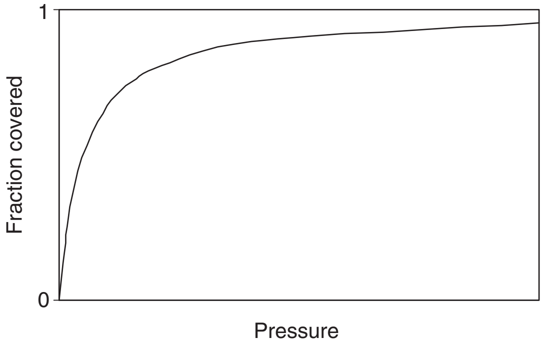

FIGURE 4.5 The Langmuir isotherm for adsorption.

Taking the reciprocal of both sides of Eq. (4.142) gives

$$\frac{1}{f} = \frac{1 + KP}{KP} = 1 + \frac{1}{KP} \tag{4.143}$$

Therefore, when $1/f$ is plotted vs. $1/P$, a straight line having a slope of $1/K$ and an intercept of 1 results, as is shown in Figure 4.6.

The volume of gas adsorbed is proportional to the fraction of the surface covered,

$$V = V_o f \tag{4.144}$$

If the maximum volume adsorbed, V_m, represents complete coverage of the surface,

$$V_m = V_o A \tag{4.145}$$

If we let the area be equal to unity (a unit area), then $A = 1$ and $V/V_m = f$. Therefore,

$$\frac{V}{V_m} = f = \frac{KP}{1 + KP} \tag{4.146}$$

which is another form of the Langmuir isotherm. This relationship provides the basis for the volumetric measurement of the number of moles of gas adsorbed as a function of gas pressure.

If two gases, A and B, are being adsorbed, the fraction of the surface area that remains uncovered is $1 - f_A - f_B$. If we describe the rate of condensation of A in terms of a rate constant for condensation, k_c, as

$$\text{Condensation rate} = k_c P_A (1 - f_A - f_B) \tag{4.147}$$

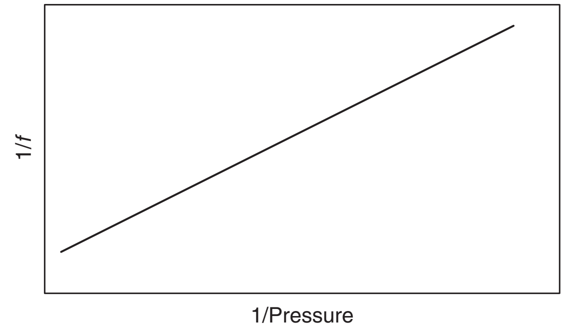

FIGURE 4.6 A reciprocal plot for the Langmuir isotherm.

and the rate of evaporation of A can be expressed in terms of the rate constant for evaporation, k_e, as

$$\text{Evaporation rate} = k_e f_A \tag{4.148}$$

at equilibrium the rates will be equal so we can write

$$k_e f_A = k_c P_A (1 - f_A - f_B) \tag{4.149}$$

or, since k_c/k_e is the equilibrium constant for adsorption, K_A, we obtain the relationship

$$K_A P_A = \frac{f_A}{1 - f_A - f_B} \tag{4.150}$$

For gas B, the corresponding equation is

$$K_B P_B = \frac{f_B}{1 - f_A - f_B} \tag{4.151}$$

Therefore, the fraction covered by A and B can be found by solving these equations for f_A and f_B. We will illustrate this procedure by solving for f_A.

Equation (4.150) can be written as

$$f_A = K_A P_A (1 - f_A - f_B) = K_A P_A - f_A K_A P_A - f_B K_A P_A \tag{4.152}$$

Solving this equation for f_B gives

$$f_B = \frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} \tag{4.153}$$

Equation (4.151) can be written as

$$f_B = K_B P_B (1 - f_A - f_B) \tag{4.154}$$

Therefore, substituting the value for f_B shown in Eq. (4.153), Eq. (4.154) becomes

$$\frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} = K_B P_B \left[1 - f_A - \frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} \right] \tag{4.155}$$

Collecting terms in the brackets over a common denominator gives

$$\frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} = K_B P_B \left[\frac{K_A P_A - f_A K_A P_A - K_A P_A + f_A K_A P_A + f_A}{K_A P_A} \right] \tag{4.156}$$

Multiplying both sides of this equation by K_AP_A and simplifying yields

$$K_AP_A - f_AK_AP_A - f_A = f_AK_BP_B \tag{4.157}$$

Modifying this equation by collecting terms containing f_A and factoring out f_A leads to

$$f_A(1 + K_AP_A + K_BP_B) = K_AP_A \tag{4.158}$$

This equation can be solved for f_A to give

$$f_A = \frac{K_AP_A}{1 + K_AP_A + K_BP_B} \tag{4.159}$$

By analogous procedures, it is possible to show that

$$f_B = \frac{K_BP_B}{1 + K_AP_A + K_BP_B} \tag{4.160}$$

If the pressure of gas B is 0 or if B interacts weakly with the adsorbent so that $K_B \approx 0$, Eq. (4.159) reduces to

$$f_A = \frac{K_AP_A}{1 + K_AP_A} \tag{4.161}$$

which is equivalent to Eq. (4.142) shown earlier for the adsorption of a single gas.

4.6.2 B–E–T Isotherm

The relationship between extent of adsorption and gas pressure shown in Figure 4.5 is by no means the only relationship known. Strictly, it applies only when maximum adsorption results in a monolayer of adsorbate on the surface. Two of the other observed types of adsorption behavior are shown in Figure 4.7.

These processes are associated with the formation of multilayers of adsorbate. The equation that can be derived to describe the formation of multilayers is

$$\frac{P}{V(P^o - P)} = \frac{1}{V_mc} + \left(\frac{c-1}{V_mc}\right)\frac{P}{P^o} \tag{4.162}$$

where V is the volume of adsorbed gas at standard conditions, P and T are the pressure and temperature of the gas, P^o is the saturated vapor pressure of the adsorbate, V_m is the volume of adsorbate at standard conditions required

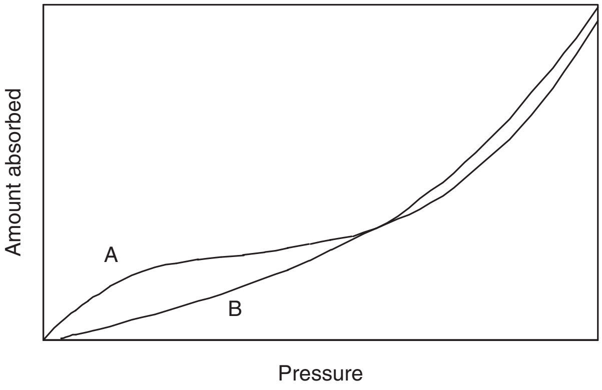

FIGURE 4.7 Adsorption isotherms for a case where there is formation of multilayers.

to give a monolayer, and c is a constant. This equation, known as the *B–E–T isotherm*, is named after Brunauer, Emmett, and Teller, who developed it. The constant c is related to the heat of adsorption of a monolayer, E_{ad}, and the heat of liquefaction of the gas, E_{liq}, by the relationship

$$c = e^{-(E_{ad}-E_{liq})/RT} \tag{4.163}$$

An adsorption isotherm of the type shown as Curve A in Figure 4.7 results when $E_{ad} > E_{liq}$, and an isotherm of the type shown as Curve B in Figure 4.7 corresponds to the case where $E_{liq} > E_{ad}$. While the B–E–T approach is more successful in dealing with more complex adsorption cases, we need not discuss its application further. Details on the derivation and use of the equation can be found in the book by White (1990).

4.6.3 Poisons and Inhibitors

For many catalysts, the presence of very small amounts of certain substances greatly reduces the effectiveness of the catalysts. These substances are usually designated as *poisons* or *inhibitors*. In some cases, the action of the poison persists only as long as the poison is present in contact with the catalyst. The poison may be one of the products of the reaction, in which case the concentration or pressure of the substance appears in the denominator of the rate law. The poison is adsorbed more strongly than the reactants, but once it is removed the catalyst recovers its activity.

Permanent catalyst poisoning occurs when some material reacts with the catalyst to form a chemically altered surface that no longer retains catalytic

properties. A wide range of cases of this type exist. Compounds containing silicon, lead (do not use lead-containing gasoline in an automobile with a catalytic converter!), sulfur, arsenic, phosphorus, etc., along with H_2S and CO, are particularly effective poisons toward metallic catalysts. Some of these poisons also inhibit enzyme action and are toxic to animals as well (Chapter 6).

Figure 4.4 shows a poison atom or molecule occupying a site on a solid catalyst. Because of that interaction, there is a very small residual potential for binding an adsorbate. Figure 4.4 is in some ways misleading in that not every surface atom is an active site. The fact that very small amounts of poisons can destroy catalytic activity suggests that the catalytic activity is confined to a rather small fraction of the total surface. In some cases, it has been found that the active sites are associated with metal atoms in an environment where there are highly unsaturated forces such as for the atoms along a ridge, crack, or pore.

We saw earlier that when a second gas is competing with the reactant for the active sites on the catalyst the fraction of the catalyst covered by the reactant (A) was decreased. If the inhibitor or poison is designated as X, we find

$$f_A = \frac{K_A P_A}{1 + K_A P_A + K_X P_X} \tag{4.164}$$

If the inhibitor has a large equilibrium constant for adsorption, $1 + K_X P_X >> K_A P_A$ and

$$f_A \approx \frac{K_A P_A}{1 + K_X P_X} \tag{4.165}$$

the rate of the reaction of A (represented as R) will be kf_A, or

$$R \approx \frac{kK_A P_A}{1 + K_X P_X} \tag{4.166}$$

and at sufficiently high pressures of X, $K_X P_X >> 1$, so the rate expression reduces to

$$R \approx \frac{kK_A P_A}{K_X P_X} \tag{4.167}$$

While the reaction is first-order in reactant A, the rate law contains the inhibitor function in the denominator, showing that the rate is decreased as the amount of inhibitor increases, in accord with the assessment presented earlier.

4.7 CATALYSIS

In reactions that are catalyzed by solid surfaces, it is the amount of *adsorbed* gas that determines the rate of the reaction. Therefore, the rate is proportional to the fraction of active sites covered, f.

$$\text{Rate} = kf \tag{4.168}$$

From the Langmuir isotherm (Eq. (4.142)), we determine that

$$\text{Rate} = k\frac{\text{KP}}{1 + \text{KP}} \tag{4.169}$$

If the reactant gas is one that is strongly adsorbed or if the pressure of the gas is high, the fraction of the surface covered approaches unity and KP >> 1, so

$$\text{Rate} = kf \approx k \tag{4.170}$$

Therefore, the rate is independent of the pressure of the reacting gas and the reaction appears to be zero-order.

When the gas is only weakly adsorbed or the pressure is low, 1 >> KP and

$$\text{Rate} = \frac{k\text{KP}}{1 + \text{KP}} \approx k\text{KP} \tag{4.171}$$

which shows the reaction to be first-order in the gaseous reactant. Figure 4.8 shows the behavior of reaction kinetics in these two limiting cases.

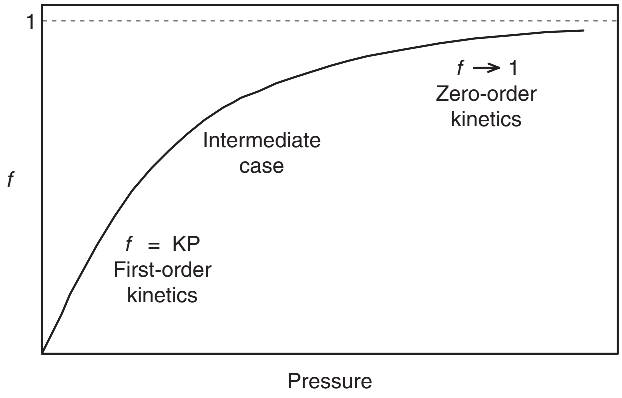

FIGURE 4.8 Kinetics of surface reactions based on the Langmiur adsorption isotherm.

In many instances, the progress of a gaseous reaction can be followed by the change in pressure of the reacting gas. If the reactant is A and its pressure is P_A, the rate equation for a first-order process is

$$-\frac{dP_A}{dt} = k'P_A \tag{4.172}$$

where $k' = kK$. By integration of this equation, we obtain

$$\ln\frac{P_{A,o}}{P_A} = k't \tag{4.173}$$

Such a rate law has been found to correctly model many reactions taking place on solid surfaces.

In the case where the gas is strongly adsorbed or the pressure is high, the process may follow a zero-order rate law. From Eq. (4.172), we see that the rate law can be written as

$$-\frac{dP_A}{dt} = k \tag{4.174}$$

which can be integrated to give

$$P_{A,o} - P_A = kt \tag{4.175}$$

This zero-order rate law has been found to correctly model the reaction of certain gases on the surfaces of solids.

Unfortunately, there are cases where neither of the limiting rate laws adequately represents the reaction as is illustrated in Fig. 4.8. For such intermediate cases,

$$\text{Rate} = kf = k\frac{KP}{1 + KP} \tag{4.176}$$

For a reactant A, the change in pressure of the gas can be used to measure the rate so that

$$-\frac{dP_A}{dt} = \frac{kKP_A}{1 + KP_A} \tag{4.177}$$

Rearranging this equation gives

$$-\frac{(1 + KP_A)}{KP_A}dP_A = k\ dt \tag{4.178}$$

which can also be written as

$$-\frac{dP_A}{KP_A} - dP_A = k\ dt \tag{4.179}$$

This equation can be simplified further before integration to give

$$\frac{1}{K} \cdot \frac{dP_A}{P_A} - dP_A = k\ dt \tag{4.180}$$

This equation must be integrated between the limits of $P_{A,o}$ at time equals zero and P_A at time t. Therefore, integration of Eq. (4.180) leads to

$$-\frac{1}{K}(\ln P_A - \ln P_{A,o}) - (P_A - P_{A,o}) = kt \tag{4.181}$$

which also can be written as

$$\frac{1}{K} \ln \frac{P_{A,o}}{P_A} + (P_{A,o} - P_A) = kt \tag{4.182}$$

The similarity of this equation to Eq. (6.26) should be noted, since these equations illustrate the similarity between reactions of adsorbed gases on solids and substrates bound to enzyme active sites in enzyme catalysis.

It is also possible to perform kinetic analysis of reactions involving adsorption of gases on solids by representing the fraction of the surface-covered means of the *Freundlich isotherm*,

$$f = kP^n \tag{4.183}$$

where f is the fraction of the surface covered, P is the pressure of the gas, and k and n are constants. Rate laws for the intermediate cases (such as those that appear to be zero-order or first-order depending on the conditions) can be developed using this approximation.

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PROBLEMS

1. Unimolecular decompositions can appear to be first- or second-order under certain conditions. What assumptions were applied to the solution of this problem? Write out the mechanism for the unimolecular decomposition of X(*g*) and derive the rate law. Explain how this rate law accounts for the observations on reaction order.

2. Suppose that a reaction follows the scheme

$$X \xrightarrow{k_1} R\bullet$$

$$R\bullet + X \xrightarrow{k_2} P + 2\ R\bullet$$

$$R\bullet \xrightarrow{k_3} Z$$

What is a reaction scheme like this called? Derive the rate expression giving [R•] as a function of time. Using your derived rate expression, explain what can happen when the concentration of X is varied between rather wide limits. What type of chemical event does this correspond to?

3. Consider the decomposition of CH_3CHO into CH_4 and CO, which is believed to take place in the steps

$$CH_3CHO \xrightarrow{k_1} CH_3\bullet + CHO$$

$$CH_3\bullet + CH_3CHO \xrightarrow{k_2} CH_4 + CO + CH_3\bullet$$

$$2\ CH_3\bullet \xrightarrow{k_3} C_2H_6$$

Use the steady state approximation to derive the rate law for the formation of CH_4. What would the rate of formation of CO be?

4. The rate of the reaction

$$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$$

is increased by electromagnetic radiation. Assuming that the radiation rapidly separates I_2 into I• and that the equilibrium

$$I\bullet + H_2(g) \rightleftharpoons IH_2(g)$$

is reached rapidly, the slow step in the process is believed to be

$$IH_2 + I(g) \rightarrow 2\ HI(g)$$

Show that this mechanism is consistent with a rate law of the form

$$\text{Rate} = k[H_2][I_2]$$

5. For the reaction

$$2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2$$

one possible mechanism is

$$NO_2Cl \rightarrow NO_2 + Cl$$

$$Cl + NO_2Cl \rightarrow NO_2 + Cl_2$$

The observed rate law is Rate = $[NO_2Cl]$. What does this tell about the mechanism?

6. Derive the rate law for the process represented by the following mechanism.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + X\ \text{(fast)}$$

$$X + D \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E\ \text{(fast)}$$

$$E \longrightarrow F\ \text{(slow)}$$

7. Consider the reaction scheme

$$NO(g) + H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2ON(g)\ \text{(fast)}$$

$$H_2ON(g) + NO(g) \xrightarrow{k_2} N_2(g) + H_2O_2(g) \text{ (slow)}$$

$$H_2O_2(g) + H_2(g) \xrightarrow{k_3} 2H_2O(g) \text{ (fast)}$$

Write the rate law for the overall reaction in terms of the steps just given. Apply the steady state approximation and obtain the final rate law.

8. The reaction between H_2 and Br_2 has been described in terms of these steps:

$$Br_2 \xrightarrow{k_1} 2Br\bullet$$

$$Br\bullet + H_2 \xrightarrow{k_2} HBr + H\bullet$$

$$H\bullet + Br_2 \xrightarrow{k_3} HBr + Br\bullet$$

$$H\bullet + HBr \xrightarrow{k_4} H_2 + Br\bullet$$

Write the rate laws for the change in concentration of H•, Br•, and HBr with time. Apply the steady state approximation and show that the rate of formation of HBr is

$$\frac{d[HBr]}{dt} = \left(\frac{k_1}{k_{-1}}\right)^{1/2} \frac{2k_2[H_2][Br_2]^{1/2}}{1 + \frac{k_4}{k_3}\frac{[HBr]}{[Br_2]}}$$

9. For each of the following, use the Langmuir isotherm and provide an interpretation for the observation. (a) The decomposition of gas X on solid S is zero-order. (b) The decomposition of gas Y on solid S is first-order. (c) The decomposition of NH_3 on a platinum surface is inversely proportional to the pressure of H_2 and directly proportional to the pressure of NH_3.

10. The reaction of NO(*g*) with $Br_2(g)$ produces ONBr(*g*) and may take place in the steps

$$NO(g) + Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ONBr_2(g) \quad \text{(fast)}$$

$$ONBr_2(g) + NO(g) \xrightarrow{k_2} 2ONBr(g) \quad \text{(slow)}$$

Assuming that $ONBr_2(g)$ establishes a steady state concentration, derive the rate law for the production of $ONBr(g)$.

11. Suppose a gaseous reaction takes place in the steps

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$B + C \xrightarrow{k_2} D$$

Derive the rate law for the formation of D and show the limiting forms at high pressure and low pressure.

12. The decomposition of tetraborane-10, B_4H_{10}, is thought to take place in the following steps (Bond, A. C., Pinsky, M. L., *J. Am. Chem. Soc.* 1970, *92*, 32).

$$B_4H_{10} \xrightarrow{k_1} B_3H_7 + BH_3$$

$$B_3H_7 \xrightarrow{k_2} BH_2 + B_2H_5$$

$$B_2H_5 \xrightarrow{k_3} BH_2 + BH_3$$

$$BH_2 + B_4H_{10} \xrightarrow{k_4} B_4H_9 + BH_3$$

$$B_4H_9 \xrightarrow{k_5} B_2H_5 + B_2H_4$$

$$B_2H_4 \xrightarrow{k_6} H_2 + \text{solid product}$$

$$2\ BH_2 \xrightarrow{k_7} B_2H_4$$

$$2\ BH_3 \xrightarrow{k_8} B_2H_6$$

Make the steady state assumption regarding BH_2,BH_3,B_2H_4,B_2H_5, B_3H_7, and B_4H_9, and show that the rate law is

$$-\frac{d[[B_4H_{10}]}{dt} = k_1[B_4H_{10}] + \frac{k_4(2k_1)^{1/2}}{k_7^{1/2}}[B_4H_{10}]^{3/2}$$

13. The decomposition of N_2O_5 is believed to involve the following steps.

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{k_3} 2\ NO_2$$

By making use of the steady state approximation with regard to the concentrations of the intermediates NO_3 and NO, derive the rate law for this process.

CHAPTER 5

Reactions in Solutions

There are many gaseous materials that react, and there are a large number of reactions that take place in the solid state. In spite of this, most chemical reactions are carried out in solutions, with a large fraction of chemistry taking place in aqueous solutions. The study of chemical kinetics must, of necessity, include a consideration of the nature of solutions and the role of the solvent in chemical processes. However, before one undertakes a description of the effects of the solvent on a reaction, it is necessary to describe some of the characteristics of liquids and solutions.

5.1 THE NATURE OF LIQUIDS

It is a relatively simple process to model many aspects of the behavior of most gases satisfactorily (except at high pressure or low temperature) using kinetic theory. For many gases, the interactions between molecules can even be ignored. The interactions between ions in ionic solids are adequately treated using Coulomb's law because the interactions are electrostatic in nature. While molecular motions in gases are random, solids have units (ions, atoms, or molecules) that are localized to fixed positions except for vibrations. Part of the problem in dealing with the liquid state is that there are intermolecular forces that are too strong to ignore, but that are not strong enough to restrict molecular motion completely. There is some local structure that results in clusters of molecules, but there is rather extensive interchange between clusters. This view of the nature of a liquid has sometimes been called the *significant structure theory* of liquids, although this term is not as frequently encountered today.

While the problem of dealing with structure and order in the liquid state is very difficult, an associated problem is that of which force law to use to

describe the intermolecular interactions. Overall, the molecules are neutral, but there may be charge separations within the molecules. Therefore, dipole-dipole forces may be the dominant type of interaction between the molecules of some liquids. On the other hand, molecules such as CCl_4 are nonpolar, so there must be an other type of force responsible for the properties of the liquid. Because the interactions between molecules in liquids provide a basis for describing the nature of solutions, we will begin this chapter with a brief discussion of intermolecular forces.

5.1.1 Intermolecular Forces

If a diatomic molecule is composed of two atoms having different electronegativities, the molecule will be polar. The shared electrons will spend a greater fraction of time in the vicinity of the atom having the higher electronegativity (CO is an exception). A measure of this charge separation is μ, the *dipole moment*, which is defined by the relationship

$$\mu = q \cdot r \tag{5.1}$$

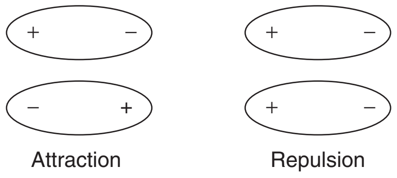
where q is the quantity of charge separated and r is the distance of separation. The quantity of charge separated will be a fraction of the electron charge (4.8×10^{-10} esu or 1.6×10^{-19} C), and the distance of separation will be on the order of 10^{-8} cm. Therefore, $q \cdot r$ will be on the order of 10^{-18} esu · cm, and it is convenient to measure μ in units of this size. This unit is known as 1 Debye in honor of Peter Debye, who did a great deal of work on polar molecules. Therefore, 10^{-18} esu · cm = 1 Debye (abbreviated as D), and these units are frequently encountered. However, when the standard units of coulombs and meters are used for charges and distances, 1 D = 3.33×10^{-30} C m.

In 1912, Keesom considered polar molecules to be assemblies of charges, although there is no *net* charge. The assembly of positive and negative charges generates an electric field that depends on the distribution of charge within the molecule. The potential energy of the interaction of the dipoles depends on their orientations. For two polar molecules having dipole moments μ_1 and μ_2, the interaction energy is given by

$$E_D = -\frac{\mu_1\mu_2}{r^3}(2\cos\theta_1\cos\theta_2 - \sin\phi_1\sin\phi_2\cos(\phi_1 - \phi_2)) \tag{5.2}$$

where θ_1, θ_2, ϕ_1, and ϕ_2 are the angular coordinates (in polar coordinates) giving the orientations of the two dipoles, and r is the average distance of

separation. The extremes of interaction (orientation) of two dipoles can be shown as



These two extremes give rise to factors of +2 and −2 for repulsion and attraction, respectively. However, there is an effect of thermal energy that prevents all of the molecules from populating the lower energy (attraction) state. The two states of unequal energy will be populated according to the Boltzmann Distribution Law. At sufficiently high temperature, the attraction is completely overcome, and the orientation of the dipoles is random. If all possible orientations between these two extremes are considered, no net attraction results. At intermediate temperatures, there is a greater population of the orientation leading to attraction, which results in some *average* preferred orientation, and a net attraction results. The orientation energy, ΔE, involves a Boltzmann population of two states of different energy, and it is, therefore, temperature dependent. It involves a factor of $e^{-E/\mathbf{k}T}$ where **k** is Boltzmann's constant (written here in bold to distinguish it from a rate constant). It can be shown that this energy varies as μ^2/r^3, and assuming that ΔE is $< \mathbf{k}T$, the equation that describes the energy of interaction of two molecules having dipole moments μ_1 and μ_2 can be written as

$$E_D = -\frac{2\mu_1^2\mu_2^2}{3r^6\mathbf{k}T} \tag{5.3}$$

If the two dipoles are identical, $\mu_1 = \mu_2$ and the equation reduces to

$$E_D = -\frac{2\mu^4}{3r^6\mathbf{k}T} \tag{5.4}$$

If the energy per mole is considered, **k** is replaced by R since **k** is R/N_o where N_o is Avogadro's number and R is the molar gas constant.

In solutions containing solutes consisting of polar molecules, the solvent strongly affects the association of the dipoles. In general, if the solvent has low polarity and/or dielectric constant, the dipoles will be more strongly associated. If the solvent is also polar, it is likely that the solvation of each polar solute molecule will be strong enough that solute molecules will be

unable to interact with each other. In other words, the interaction between molecules of the solute and solvent will compete with interactions between the solute molecules. Thus, the association of a polar solute can be shown as

$$2D \rightleftharpoons D_2 \tag{5.5}$$

for which the equilibrium constant $K = [D_2]/[D]^2$ will be strongly solvent dependent. In the same way that interactions between ions are governed by Coulomb's law, the dielectric constant of the solvent will affect the attraction between dipoles. Species that are of extreme difference in polarity may not be completely miscible owing to each type of molecule interacting strongly with molecules of its own kind. Although they are weak compared to chemical bonds, dipole-dipole forces are of considerable importance in determining chemical properties.

A permanent dipole, $\mu = q \times r$ can induce a charge separation in a neighboring nonpolar molecule that is proportional to the polarizability of the molecule. If the polarizability of the molecule is represented as α, the energy of the interaction between the permanent dipole and the nonpolar molecule with an induced dipole moment can be expressed as

$$E_I = -\frac{2\alpha\mu^2}{r^6} \tag{5.6}$$

These forces between polar molecules and those having a dipole induced in them are called *dipole-induced dipole forces*, and they are essentially temperature independent.

It should be apparent that there must be *some* force between molecules that are nonpolar because CH_4, He, CO_2, and similar molecules can be liquefied. These forces must also be electrical in nature but cannot be the result of an overall charge separation within the molecules. If we consider two helium atoms as shown in Figure 5.1, it is possible that at some instant both of the electrons in one atom will be on the same side of the atom. There is an *instantaneous* dipole that will cause an instantaneous change in

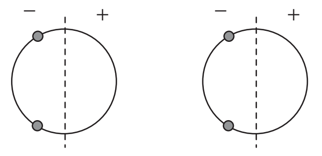


FIGURE 5.1 Two helium atoms showing the instantaneous dipoles that result in a weak force of attraction.

the electron distribution in the neighboring atom. There will exist, then, a weak force of attraction between the two atoms. Such forces between instantaneous dipoles are the *London forces* (sometimes called *dispersion forces*). They can be considered as weak forces between the nuclei in one molecule and the electrons in another.

The energy of interaction of molecules by London forces can be described by the equation

$$E_L = -\frac{3h\nu_o\alpha^2}{4r^6} \tag{5.7}$$

where ν_o is the frequency of the zero-point vibration and α is the polarizabilty of the molecule. Because $h\nu_o$ is approximately equal to the ionization energy of the molecule, I, Eq. (5.7) becomes

$$E_L = -\frac{3I\alpha^2}{4r^6} \tag{5.8}$$

If two different types of molecules are involved in the interaction, the energy is

$$E_L = -\frac{3}{2}\frac{h\alpha_1\alpha_2\nu_1\nu_2}{r^6(\nu_1+\nu_2)} \tag{5.9}$$

When expressed in terms of the ionization potentials, this equation can be written as

$$E_L = -\frac{3}{2}\frac{I_1I_2\alpha_1\alpha_2}{r^6(I_1+I_2)} \tag{5.10}$$

Although it may be somewhat surprising, many molecules of greatly differing structures have ionization potentials that are approximately the same. The examples shown in Table 5.1 include molecules of many types, but the ionization potentials do not vary much. Therefore, the product of I_1 and I_2 is sometimes replaced by a constant.

TABLE 5.1 Ionization Potentials for Selected Molecules.

Molecule	I.P. (ev)	Molecule	I.P. (ev)
Acetone	9.69	Methanol	10.85
Benzene	9.24	3-Methylpentane	10.06
n-Butane	10.63	Pyrazine	10.00
1,4-Doxane	9.13	Sulfur dioxide	11.7

Slater and Kirkwood have derived an expression for the London energy that makes use of the number of outermost electrons in the molecule. This is possible because the polarizibilty of the electrons in a molecule is generally dependent on the number of electrons present. The expression derived by Slater and Kirkwood can be written as

$$E_L = -\frac{3he\alpha^2}{8\pi r^6 m^{1/2}}\left(\frac{n}{\alpha}\right)^2 \tag{5.11}$$

where e is the charge on the electron, n is the number of electrons in the outermost shell, and m is the mass of the electron.

Because the London attraction energy depends on the magnitude of α, it shows a general relationship to molecular size and number of electrons. For example, the boiling point of a liquid involves the separation of molecules from their nearest neighbors. Thus, the boiling points of a given series of compounds (e.g., the hydrocarbons, C_nH_{2n+2}) show a general increase in boiling point as n (and, hence, α) increases. Similarly, the halogens reflect this trend with F_2 and Cl_2 being gases at room temperature while Br_2 is a liquid, and I_2 is a solid. All are nonpolar, but the number of electrons increases for the series, and the polarizability depends on the ability to distort the electron cloud of the molecule. Generally, the polarizability of molecules increases as the number of electrons increases, but it is important to note that molecules that have delocalized electron density have mobile electrons. Such electron clouds can be distorted, which gives rise to a larger polarizability. These effects are generally reflected in the boiling points of the liquids. Because of this, the boiling point of benzene (C_6H_6, a total of 42 electrons and a molecular weight of 78) is very close to that of carbon tetrachloride (CCl_4, a total of 74 electrons and a molecular weight of 154). Both are nonpolar, but the π-electron system in benzene results in a relatively large polarizability while the electrons in the CCl_4 molecule are more localized.

It is also important to note that London forces also play an important role in contributing to the overall stability of crystal lattices. Even though the dominant force is the Coulombic force between oppositely charged ions, the London forces are significant in the case of large, polarizable (*soft* in terms of the hard-soft interaction principle) ions. For example, in AgI the Coulombic attraction is 808 kJ/mol and the London attraction amounts to 128.7 kJ/mol. As expected, London forces are much less important for crystals like NaF because the ions are much less polarizable. Because the London energy varies as $1/r^6$, the force decreases rapidly as r increases, and only the interactions between nearest neighbors are significant.

Various equations have been used to represent the repulsion that also exists between molecules when they are separated by short distances. One such equation is

$$E_r = a\ e^{-br} \tag{5.12}$$

where a and b are constants. One type of potential function that includes both attraction and repulsion is known as the Mie potential, which is represented by

$$E = \frac{A}{r^n} - \frac{B}{r^m} \tag{5.13}$$

where A, B, m, and n are constants. The repulsion (positive) term is often written as

$$E_r = \frac{j}{r^n} \tag{5.14}$$

where j is a constant and n has values that range from 9 to 12. The Lennard–Jones potential combines this form with a term involving $1/r^6$ for the attraction and usually uses $n = 12$ as the exponent in the repulsion term. The resulting equation is

$$E = \frac{j}{r^{12}} - \frac{k}{r^6} \tag{5.15}$$

where j and k are constants, and is referred to as the "6–12" or Lennard–Jones potential. The discussion presented here should show that London forces are important in determining properties of liquids and are significant in certain types of crystals. We can also see that there are several ways of expressing the interaction energies mathematically. In some of the discussions presented in later sections of this book, we will have opportunities to make use of qualitative applications of the ideas presented here.

5.1.2 The Solubility Parameter

It is intuitively obvious that a liquid has a certain amount of cohesion that holds the liquid together. It should also be apparent that the energy with which the liquid is held together is related to the heat necessary to vaporize it, which separates the molecules. In fact, the cohesion energy, E_c, is given by

$$E_c = \Delta H_v - RT \tag{5.16}$$

The work done as the vapor expands against the external (atmospheric) pressure is RT. The quantity E_c/V, where V is the molar volume, is called the *cohesion energy density* because it is the cohesion energy per unit volume. A basic thermodynamic relationship,

$$\Delta E = T\,dS - P\,dV \tag{5.17}$$

provides a way of interpreting the cohesion energy. From Eq. (5.17), we obtain

$$\frac{\partial E}{\partial V} = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{5.18}$$

where P is the *external pressure*. The *internal pressure* is given by

$$P_i = T\left(\frac{\partial P}{\partial T}\right)_V \tag{5.19}$$

However, we can also express the change in pressure with temperature at constant volume by making use of a well-known thermodynamic relationship,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{5.20}$$

The numerator on the right-hand side of this equation represents the coefficient of thermal expansion, α. The denominator of the equation represents the change in volume with pressure at constant temperature, which is the coefficient of compressibility, β. Therefore, the internal pressure is given by

$$P_i = T\frac{\alpha}{\beta} \tag{5.21}$$

For most liquids, the internal pressure ranges from 2000 to 8000 atm. As we will see, this has important ramifications with regard to the formation of transition states in which there is a volume change. From the foregoing development, we can now write the cohesion energy as

$$E_c = P_i - P \approx P_i \tag{5.22}$$

because the internal pressure is normally much greater than the external pressure, $P_i >> P$. In a general way, the cohesion energy and internal pressure reflect the strength of intermolecular interactions in the liquid.

The cohesion energy (*energy* of vaporization) per unit volume is obtained from E_c/V, where V is the molar volume. It can be shown that if two liquids have the same value of E_c/V, the heat of mixing is zero because they form an ideal solution. If the E_c/V values are not equal, the heat of mixing will be positive (the solution will be nonideal). However, in developing the theory of solutions, the quantity $(E_c/V)^{1/2}$ is often encountered. This quantity is known as the *solubility parameter*, δ. The solubility parameter is given in $(cal/cm^3)^{1/2}$ or in $(J/cm^3)^{1/2}$. The unit of 1 $cal^{1/2}/cm^{3/2}$ is called 1 Hildebrand, (h) in honor of Joel Hildebrand who did extensive work on the nature of solutions. Table 5.2 shows solubility parameters for several common solvents. It can be seen that the values for δ range from about 7 $(cal/cm^3)^{1/2}$ for hexane (in which only London forces exist) to about 4 times that value for a strongly associated liquid such as water where there are hydrogen bonding, dipole-dipole, and London forces.

Since the cohesion energy is given by the relationship

$$E_c = \Delta H_v - RT \tag{5.23}$$

TABLE 5.2 Solubility Parameters for Selected Liquids.

Liquid	Solubility parameter (h)	Liquid	Solubility parameter (h)
n-C_6H_{14}	7.3	CS_2	10.0
n-C_7H_{16}	7.5	CH_3CN	11.9
$(C_2H_5)_2O$	7.66	Br_2	11.5
cyclo-C_6H_{12}	8.2	C_3H_8CN	20.0
CCl_4	8.6	CH_3NO_2	12.6
C_6H_6	9.1	$C_6H_5NO_2$	11.6
$C_6H_5CH_3$	8.9	CH_3COOH	10.4
Tetrahydrofuran	9.5	*o*-$C_6H_4(CH_3)_2$	8.84
$CHCl_3$	9.3	CH_2Cl_2	9.9
$CH_3COOC_2H_5$	9.0	$HCON(CH_3)_2$	12.1
$CHCl_3$	9.3	C_2H_5OH	12.7
$(CH_3)_2CO$	9.76	CH_3OH	14.5
1,4-dioxane	10.0	C_6H_5CN	9.7
HOC_2H_4OH	16.1	H_2O	26.0

we can calculate it when ΔH_v is known. Values for the heat of vaporization of many liquids are tabulated in handbooks. However, the heat of vaporization can be obtained by using the relationship

$$\frac{d \ln P}{d(1/T)} = \Delta H_v \tag{5.24}$$

if we have the vapor pressure expressed as a function of temperature. Although there are many equations that have been used to relate vapor pressure to temperature, one of the most convenient for this use is the Antoine equation,

$$\log P = A - \frac{B}{C + t} \tag{5.25}$$

where A, B, and C are constants characteristic of the liquid and t is the temperature in °C. Antoine constants have been tabulated for a large number of liquids. However, if the vapor pressure of a liquid is known as several temperatures, the Antoine constants can be calculated. Using the Antoine equation and Eqs. (5.23) and (5.24), we find that the cohesion energy can be expressed as (the −1 term inside the parentheses provides for a subtraction of RT to correct for expansion work against atmospheric pressure)

$$E_c = RT\left(\frac{2.303BT}{(C + t)^2} - 1\right) \tag{5.26}$$

Therefore, having determined the cohesion energy, the solubility parameter can be calculated if the molar volume is known. Calculating the molar volume requires knowing the density of the liquid at the desired temperature, and the density data are usually available for most liquids. If the density, ρ, at the desired temperature is unavailable but it is available at other temperatures, the data can be fitted to the equation

$$\rho = a + bT + cT^2 \tag{5.27}$$

and the constants a, b, and c can be evaluated using a least squares method. The calculated density at the desired temperature and the molar volume can then be determined.

The cohesion of mixed solvents can be calculated by making use of the sum of the contributions of each component. Those individual contributions are determined by the product of the solubility parameter of each liquid multiplied by the mole fraction of that component. The sum of the individual contributions gives the solubility parameter for the solution.

Because the solubility parameter reflects the intermolecular forces in a liquid, it is a very useful parameter. The total interaction between molecules in a liquid may be the result of dipole-dipole, London, and hydrogen-bonding interactions. Therefore, it is possible to separate the contributions from each type of interaction and express the solubility parameter as though it were a vector sum. The result is

$$\delta^2 = \delta_L^2 + \delta_D^2 + \delta_H^2 \tag{5.28}$$

where δ_D, δ_L, and δ_H are contributions to the solubility parameter from dipole-dipole, London, and hydrogen-bonding interactions, respectively.

5.1.3 Solvation of Ions and Molecules

When an ionic compound dissolves in a polar solvent such as water, the ions become strongly solvated. The ion-dipole forces produce a layer of solvent molecules (the primary solvation sphere) surrounding each ion. This layer can cause other solvent molecules in the immediate vicinity to become oriented as well. Although the primary solvation sphere may seem to be rather firmly attached to the ion, there is considerable interchange between these molecules and the bulk solvent in a dynamic process in most cases. For strongly solvated ions like $[Cr(H_2O_6]^{3+}$, the exchange of coordinated water molecules and those of the bulk solvent is very slow. As we shall describe later, some desolvation of ionic species may be required before a reaction of the ion can take place.

The nature of solvated species is often an important consideration. For example, the symbol for the solvated proton in acidic solutions is written as H_3O^+, but the H^+ is solvated by more than one water molecule. In fact, the predominant species is probably $H_9O_4{}^+$, which is $H^+{\bullet}4H_2O$, and this ion has been identified in vapors above concentrated acids as well as a cation in solids, so it has some stability. Other species (e.g., $H_7O_3{}^+$, which is H^+ solvated by three H_2O molecules) can also exist in equilibrium with $H_9O_4{}^+$. In general, the average number of water molecules solvating an ion depends on the concentration of the ion in the solution as well as the size and charge of the ion.

Theoretical treatment of the solvation of ions is quite difficult. If we could use a simple electrostatic approach in which polar molecules interact with a charged ion, the problem would be much simpler. However, the fact that the polar solvent molecules interact with an ion causes their

character to change somewhat, and the polarity of the molecules is increased due to the induced charge separation resulting from the ion-dipole forces. Consequently, solvent molecules that are bound to an ion have a different dipole moment and dielectric constant from the bulk of the solvent. Moreover, the magnitude of the changes depends on the nature of the ion being solvated. The bound solvent molecules are essentially restricted in their ability to respond to an applied electric field, which is the phenomenon that provides the basis for measuring the electrical properties of the solvent. Therefore, the dielectric constant of the water attached to an ion is smaller than that of the bulk solvent.

When an electrostatic approach to the interaction between an ion and a polar solvent is used and the dielectric constant, ε, is assumed to be the same as the bulk solvent, the free energy of hydration (ΔG_h) of an ion of radius r can be shown to be

$$\Delta G_h = -\frac{N_o Z^2 e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \tag{5.29}$$

where Z is the charge on the ion, e is the charge on the electron, and N_o is Avogadro's number. However, agreement between calculated and experimental values of ΔG_h is usually poor. One way around this is to use an "effective" ionic radius, which is the radius of the ion plus the radius of a water molecule (about 0.75 Å or 75 nm). Another way to improve the calculation is to correct for the change in the dielectric constant that occurs when water surrounds an ion. When this approach is used, the dielectric constant is expressed as a function of the ionic radius. This is done because smaller, more highly charged ions are more strongly solvated and restrict the motion of the water molecules to a greater extent. The effective dielectric constant of a liquid changes around an ion in solution, and the higher the charge on the ion, the greater the change. This effect occurs because the dielectric constant is a measure of the ability of a molecule to orient itself in aligning with an applied electric field. Because the solvent molecules become strongly attached to an ion, they have a reduced ability to orient themselves in the electric field, so the dielectric constant is smaller than it is for the bulk solvent. Consequently, the reduction in dielectric constant is greater the closer the solvent molecules get to the ion and the higher the charge on the ion. The principles related to solvation are important in interpreting the role of the solvent in kinetic studies because solvation of both reactants and the transition state must be considered.

5.1.4 The Hard-Soft Interaction Principle (HSIP)

We have already alluded to one of the most useful and pervasive principles in all of chemistry, that being the hard-soft interaction principle (HSIP). This principle relates to many areas, but it is most directly applicable to interactions in which there is electron pair donation and acceptance (Lewis acid-base interactions). The terms *hard* and *soft* relate essentially to the polarizability of the interacting species. For example, I^- has a large size, so its electron cloud is much more distortable than that of F^-. Likewise, Hg^{2+} is a large metal ion having a low charge, while Be^{2+} is a very small ion. The result is that Hg^{2+} is considered to be a soft Lewis acid while Be^{2+} is considered to be a hard Lewis acid. As a result of these characteristics, Hg^{2+} interacts preferentially with I^- rather than F^-, while Be^{2+} interacts preferentially with F^-. The hard-soft interaction principle indicates that *species of similar electronic character (hard or soft) interact best.* It does *not* say that hard Lewis acids will *not* interact with soft Lewis bases, but the interaction is *more favorable* when the acid and base are similar in hard-soft character.

The applications of the hard-soft interaction principle are numerous. For example, if we consider the potential interaction of H^+ with either H_2O or I^-, where does H^+ go?

$$H_2O \xleftarrow{?} H^+ \xrightarrow{?} I^-$$

We find that H^+, being a hard acid (electron pair acceptor), interacts preferentially with a pair of electrons in a small orbital on the oxygen atom rather than the pair of electrons in a large orbital on I^-. Accordingly, HI is completely ionized in dilute aqueous solutions as a result of the protons being transferred to H_2O. However, it must be emphasized that such a proton transfer from HI to H_2O is energetically unfavorable in the gas phase. The extremely high heat of solvation of H^+ makes this reaction take place in solutions, so the process is not quite as simple as shown earlier.

If we consider the competition between F^- and H_2O for H^+,

$$H_2O \xleftarrow{?} H^+ \xrightarrow{?} F^-$$

we find that the pairs of electrons on F^- and those on the oxygen atom in a water molecule are contained in orbitals of similar size. Furthermore, the negative charge on the F^- increases the attraction between H^+ and F^-. As a result, in aqueous solution, H^+ interacts more strongly with F^- than with H_2O, and, therefore, HF ionizes only slightly in water and behaves as a weak acid. Further, if we consider the complex formed between Pt^{2+}

(low charge, large size, soft electron pair acceptor) and SCN^-, it is found that the bonding is Pt^{2+}—SCN. The complex of Cr^{3+} (small size, high charge, hard electron pair acceptor) has the bonding arrangement Cr^{3+}—NCS. These results arise because the sulfur end of SCN^- is considered to be a soft electron pair donor, while the nitrogen end behaves as a hard electron pair donor.

The primary reason for discussing the hard-soft interaction principle at this time is because of its usefulness in dealing with solubility and solvation. Certainly, the principle "like dissolves like" has been known for a very long time. We will mention here only a few aspects of the HSIP and its relationship to solubility. As an example, we can consider that NaCl is essentially insoluble in nitrobenzene ($\mu = 4.27D$). Even though nitrobenzene is quite polar, it can not solvate ions like Na^+ or Cl^- because of the size of the molecules. It is polar, but μ depends on both the quantity of charge separated and the distance of separation. Since nitrobenzene is a large molecule, its size causes the dipole moment to be large, but it also limits the ability of the molecules to solvate small ions.

The solubility of NaCl in water and alcohols also shows an interesting trend and allows us to see the effects of solvent properties. The relevant data are shown in Table 5.3. As the size of the solvent molecules increases and the dielectric constant decreases, the solubility of NaCl decreases. The size and character of the alkyl group becomes dominant over that of the polar OH group. Accordingly, the solubility of ionic solids such as NaCl decreases with increasing size of the alkyl group.

It has long been known (and utilized) that liquid SO_2 will dissolve aromatic hydrocarbons. The resonance structures for SO_2 can be shown as

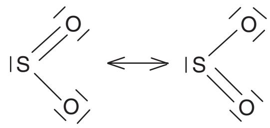


TABLE 5.3 Solubility of NaCl in Water and Alcohols.

Solvent	H_2O	CH_3OH	C_2H_5OH	n–C_3H_7OH
Solubility, mole percent	10.0	0.772	0.115	0.00446
Dipole moment, D	1.84	1.66	1.66	1.68
Dielectric constant, ε	78.5	24.6	20.1	18.3

and they show that the molecule has delocalized electron density due to the π-bonding. There is also delocalized electron density in aromatic hydrocarbon molecules. Therefore, the similarity between the electronic character of SO_2 and aromatic hydrocarbon molecules results in the hydrocarbons being soluble in liquid SO_2. In contrast, aliphatic hydrocarbons are essentially insoluble in liquid SO_2, so the difference in solubility allows aliphatic and aromatic hydrocarbons to be separated by an extraction process using liquid SO_2 as the solvent.

While we have barely introduced the applications of the HSIP (often referred to as HSAB when acid-base chemistry is the focus), the suggested readings at the end of this chapter can be consulted for additional details. A great deal of what will be discussed later about the solvation of reactants and transition states can be reduced to applications of this very important and versatile principle, which was first systematized by Ralph G. Pearson in the 1960s.

5.2 EFFECTS OF SOLVENT POLARITY ON RATES

We have already described briefly some of the effects of dipole-dipole association. For example, the more strongly solvated an ion or molecule is, the more difficult it is for desolvation to occur so that an active site is exposed. Reactions in which ions are *produced* as the transition state forms from reactants will usually *be accelerated as the solvent dielectric constant and dipole moment increase for a series of solvents*. The increased solvation of the ions that constitute the transition state will cause this effect. In contrast, *reactions that involve the combination of ions to produce a transition state of low charge will be retarded by solvents that strongly solvate ions*. In order for the ions to combine, they must be separated from the solvent molecules, which is energetically unfavorable.

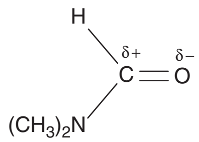
It is generally true that the formation of a transition state involves some change in the distribution of charges in the reactants. Neutral molecules frequently have charge separations induced (see Section 1.5.3), but in other cases forming a transition state during the reaction of ionic species involves cancellation or rearrangement of some portion of the charges.

An early attempt to explain these factors was put forth by Sir Christopher Ingold and his coworkers in 1935. The cases considered involve *charge neutralization* as positive and negative ions react and *charge dispersion* as a

positive or negative ion has part or all of its charge spread over the transition state. In cases involving charge neutralization, the rate of the reaction *decreases* when the reaction is carried out in a series of solvents of *increasing* polarity. It is more favorable energetically for the ions to remain separated and solvated by the polar solvent than to form a transition state that has the charges dispersed or cancelled.

On the other hand, a reaction in which a molecule having a symmetric charge distribution forms a transition state having some charge separation will have a rate that *increases* with solvent polarity. As the charged regions are formed, they interact favorably with the polar molecules of the solvent. This is sometimes referred to as *solvent-assisted formation of the transition state.* It must be remembered, however, that dipole moment alone is not always a good predictor of solvent behavior toward ions. For example, nitrobenzene is quite polar, but it is a very poor solvent for materials containing small ions (e.g., NaCl) because of the size of the nitrobenzene molecules. The dipole moment is the product of the amount of charge separated and the distance of separation. Therefore, a rather large value for μ could be the result of a small amount of charge being separated by a rather large distance. Molecules having those characteristics would not be good solvents for ionic salts containing small ions.

Some solvents consisting of polar molecules solvate anions and cations to different degrees because of their molecule structure. For example, *N*,*N*-dimethylformamide is polar,



but the positive end of the dipole is shielded to the extent that it is not as accessible for solvating anions as is the negative end for solvating cations. This is also true for solvents such as $(CH_3)_2SO$ and CH_3CN. All are fairly good solvents for polar or ionic compounds. Because the negative end of the dipole is less shielded than is the positive end, cations tend to be more strongly solvated than are anions in these solvents. The weaker solvation of the anions results in their being able to react readily in reactions such as nucleophilic substitution in those solvents, and the rates are usually higher than when a solvent such as CH_3OH is used. Methanol can solvate both cations and anions about equally well.

TABLE 5.4 Relative Rates of the Reaction Shown in Eq. (5.30) in Several Solvents (Ege, 1994).

Solvent	Relative rate
CH_3OH	1
$HCONH_2$	1.25
$HCON(CH_3)_2$	1.2×10^6
$(CH_3)CON(CH_3)_2$	7.4×10^6

The rate of the reaction

$$CH_3I + Cl^- \rightarrow CH_3Cl + I^- \tag{5.30}$$

shows such a dependence, and the relative rates of the reactions in several solvents are shown in Table 5.4. For the series of solvents shown, the reaction rate increases as the ability of the solvent to solvate anions decreases. Since the reaction involves an anion, strongly solvating the anion decreases the rate of substitution.

The data show that as the size of the solvent molecule increases, the solvent is less able to solvate the ion that is the entering group and the rate of the reaction increases. The number of cases where similar observations on solvent effects are encountered is enormous. Later in this chapter, those principles will be extended to include the effects that result from using solvents that have different solubility parameters.

5.3 IDEAL SOLUTIONS

The thermodynamic behavior of *real* solutions, such as those in which most reactions take place, is based on a description of *ideal* solutions. The model of an ideal solution is based on Raoult's law. While we can measure the concentration of a species in solution by its mole fraction, X_i, the fact that the solution is not ideal tells us that thermodynamic behavior must be based on fugacity, f_i. In this development, we will use f_i as the fugacity of the pure component i and $\mathbf{f}_i$ as the fugacity of component i in the solution. When X_i approaches unity, its fugacity is given by

$$\mathbf{f}_i = X_i f_i \tag{5.31}$$

This is expressed by the relationship known as the *Lewis and Randall rule* which can be stated as,

$$\lim_{X_i \to 1} \left(\frac{\mathbf{f}_i}{X_i} \right) = f_i \tag{5.32}$$

When X_i approaches zero, the limit of $\mathbf{f}_i / X_i$ approaches a constant, C, which is known as Henry's constant.

$$\lim_{X_i \to 0} \left(\frac{\mathbf{f}_i}{X_i} \right) = C_i \tag{5.33}$$

When a solution behaves ideally, $\mathbf{f}_i = C_i$ for all values of X_i. This means that we can write

$$\mathbf{f}_i = X_i f_i^o \tag{5.34}$$

where f_i^o is the fugacity of the standard state of component i. Usually, f_i^o is taken as the fugacity of the pure component i at the temperature and pressure of the solution.

When a solution is formed by mixing two components, the properties of the mixture (the solution) are related to those of the individual components and the composition of the solution. For example, the change in volume is described as

$$\Delta V = V_{actual} - \sum X_i V_i^o \tag{5.35}$$

where V_i^o is the molar volume of pure component i in its standard state. If we represent some property, $\mathbf{P}$, in terms of the molar properties of the components, P_i, we obtain

$$\mathbf{P} = \sum X_i P_i \tag{5.36}$$

Therefore, the *change* in the property upon mixing the components can be represented by the equation

$$\Delta \mathbf{P} = \sum X_i (P_i - P_i^o) \tag{5.37}$$

where P_i^o is the property of the standard state of component i. When the property considered is the free energy, the equation becomes

$$\Delta G = \sum X_i (G_i - G_i^o) \tag{5.38}$$

Using the relationship that

$$\Delta G = RT \ln \left(\frac{\mathbf{f}_i}{f_i^o} \right) \tag{5.39}$$

we see that mixing causes a change in free energy that is given by

$$\Delta G = RT \sum X_i \ln\left(\frac{\mathbf{f}_i}{f_i^o}\right) \tag{5.40}$$

The ratio ($\mathbf{f}_i/f_i^o$) is the *activity* of component i in the solution. For a pure component ($X_i = 1$), the activity of the component in its standard state is given by

$$a_i = \frac{\mathbf{f}_i}{f_i^o} \tag{5.41}$$

Since the fugacity of component i in an ideal solution is $\mathbf{f}_i = X_i f_i^o$, we can write

$$a_i = \frac{\mathbf{f}_i}{f_i^o} = \frac{X_i f_i^o}{f_i^o} = X_i \tag{5.42}$$

which shows that the activity of component i can be approximated as the mole fraction of i, which is equal to X_i. Therefore, Eq. (5.40) becomes

$$\Delta G = RT \sum X_i \ln X_i \tag{5.43}$$

or

$$\frac{\Delta G}{RT} = \sum X_i \ln X_i \tag{5.44}$$

In a similar way, it can be shown that because the composition of an *ideal* solution is independent of temperature,

$$\frac{\Delta H}{RT} = -\sum X_i \left(\frac{\partial \ln X_i}{\partial T}\right)_{P,X} = 0 \tag{5.45}$$

The subscript X after the partial derivative is for $X \neq X_i$. This equation indicates that the heat of solution for an *ideal* solution is zero. The entropy of solution can be shown to be

$$\frac{\Delta S}{R} = -\sum X_i \ln X_i \tag{5.46}$$

It is apparent that one of the criteria for the mixture being ideal is that $\Delta H_{mixing} = 0$. However, ΔG_{mixing} and $T\Delta S_{mixing}$ are not zero, but they are equal and opposite in sign because $\Delta G = \Delta H - T\Delta S$. The relationships of the thermodynamic quantities to composition for an ideal solution are shown in Figure 5.2.

Real solutions are described in terms of the *difference* between the experimental value for a property and that which would result for an

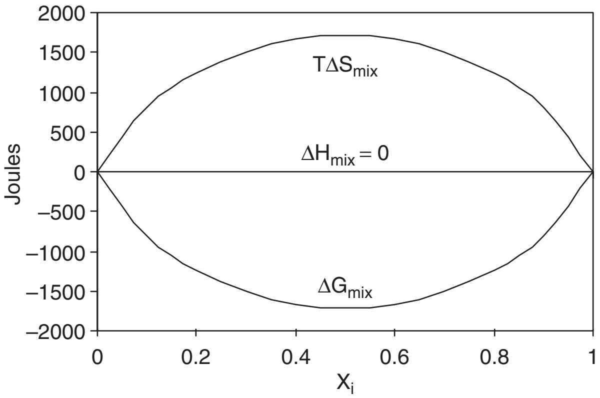


FIGURE 5.2 Relationship between the composition of an ideal solution and the thermodynamic quantities.

ideal solution at the same conditions. These differences are referred to as the *excess property*, P^E

$$P^E = P_{measured} - P_{ideal} \tag{5.47}$$

or

$$\Delta P^E = \Delta P_{measured} - \Delta P_{ideal} \tag{5.48}$$

The excess properties (such as excess volume) are important in describing solutions in thermodynamic terms.

5.4 COHESION ENERGIES OF IDEAL SOLUTIONS

If the forces between molecules are of the van der Waals type, it can be shown that the internal pressure, P_i, is given by the change in energy with volume at constant temperature.

$$\left(\frac{\partial E}{\partial V}\right)_T = P_i = \frac{a}{V^2} \tag{5.49}$$

where a/V^2 is the same quantity that appears in the van der Waals equation,

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{5.50}$$

Although the terms *cohesion energy density* and *internal pressure* refer to the same characteristic of a liquid, they are not identical. The cohesion energy density (E_c/V) is equivalent to the energy of vaporization per mole of liquid and it is calculated in that way. The internal pressure, P_i, is given by

$$P_i = \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \tag{5.51}$$

Since it can be shown from thermodynamics that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{5.52}$$

the internal pressure is determined from measurements of the change in pressure with temperature at constant volume. Although P_i and E_c/V are not identical, they produce similar effects on the rates of reactions, so the terms are used somewhat interchangeably. For conditions where the internal pressure and the cohesion energy density are of equal magnitudes,

$$\frac{E_c}{V} = P_i = \frac{a}{V^2} \tag{5.53}$$

For a mixture of components 1 and 2, the cohesion energy for the mixture, E_{cm}, will be given by

$$E_{cm} = \frac{a_m}{V_m} \tag{5.54}$$

If we represent the mole fraction of component 1 as X_1, then $X_2 = (1 - X_1)$ and the value of a_m is

$$a_m = X_1^2 a_1 + 2X_1(1 - X_1)a_{12} + (1 - X_1)^2 a_2 \tag{5.55}$$

where the interaction between components 1 and 2 is given in terms of the van der Waals constants by

$$a_{12} = (a_1 a_2)^{1/2} \tag{5.56}$$

This relationship is often referred to as the Bertholet geometric mean. If no change in volume occurs when the mixture is formed,

$$V_m = X_1 V_1 + (1 - X_1)V_2 \tag{5.57}$$

The cohesion energy of the mixture, E_{cm}, is given in terms of the mole fractions (X) and cohesion energies of the two components by

$$E_{cm} = X_1 E_{c1} + (1 - X_1)E_{c2} \tag{5.58}$$

The change in cohesion energy when the mixture forms compared to the cohesion energy of the two components is

$$\Delta E_c = \frac{X_1(1 - X_1)V_1V_2}{X_1V_1 + (1 - X_1)V_2}\left(\frac{\sqrt{a_1}}{V_1} - \frac{\sqrt{a_2}}{V_2}\right)^2 \tag{5.59}$$

This equation is known as the *Van Laar equation*. Considering the interaction between the molecules of the liquids as resulting from van der Waals forces, the cohesion energy density is

$$\frac{E_c}{V} = \frac{a}{V^2} \tag{5.60}$$

Therefore,

$$\Delta E_c = \frac{X_1(1 - X_1)V_1V_2}{X_1V_1 + (1 - X_1)V_2}\left[\left(\frac{E_{c1}}{V_1}\right)^{1/2} - \left(\frac{E_{c2}}{V_2}\right)^{1/2}\right]^2 \tag{5.61}$$

This equation is known as the *Hildebrand–Scatchard equation*. Of course $(E_c/V)^{1/2}$ is the solubility parameter, δ, so we can write this equation as

$$\Delta E_c = \frac{X_1(1 - X_1)V_1V_2}{X_1V_1 + (1 - X_1)V_2}[\delta_1 - \delta_2]^2 \tag{5.62}$$

Thus, the difference in solubility parameters between the solvent and solute determines a great deal about the character of the solution. For example, water and carbon tetrachloride have cohesion energies that are approximately equal. However, the cohesion in water is the result of dipole-dipole forces and hydrogen bonding, while that in carbon tetrachloride is due to London forces. Mixing the two liquids would result in a heat of mixing being positive because the strong interactions within the two components is not offset by forces that result between the polar and nonpolar molecules. Therefore, the two liquids do not mix. In some cases, the failure of the liquids to mix is due to an unfavorable change in entropy.

We need now to consider other aspects of the process of forming a solution from two components. We will represent the partial molar quantities of the pure components as G_i^o, H_i^o, and E_i^o and those of the same components in solution as G_i, H_i, and E_i. The partial molar free energy, G_i, is related to that of the component in an *ideal* solution, G_i^o, by the relationship

$$G_i - G_i^o = RT \ln a_i \tag{5.63}$$

where a_i is the activity of component i. By using the analogous relationship for a *real* solution, we obtain

$$G_i - G_i^o = RT \ln \frac{a_i}{X_i} = RT \ln \gamma_i \tag{5.64}$$

where X_i is the mole fraction of component i and γ is the activity coefficient. Therefore, because

$$\Delta G = \Delta H - T\Delta S \tag{5.65}$$

we can separate the free energy into the enthalpy and entropy components,

$$(H_i - H_i^o) - T(S_i - S_i^o) = RT \ln \gamma_i \tag{5.66}$$

If molecular clustering does not occur and the orientation of each component is random in both the pure component and in the solution, the entropy of component i will be approximately the same in the solution as it is in the pure component. Therefore,

$$S_i = S_i^o \tag{5.67}$$

The change in volume of mixing the liquids is usually small, so

$$\Delta H = \Delta E + \Delta(PV) \approx \Delta E \tag{5.68}$$

If the activity coefficient is approximately unity, the energy of one mole of component i is approximately the same in the solution as it is in the pure component. A relationship of this form is of great use in describing the thermodynamics of constituents of a solution. Although we have delved rather deeply into the nature of solutions and the related thermodynamics, these topics form the basis for understanding how solvents affect the kinetics of reactions. There is a great deal of similarity between how two components interact when they form a solution and how a solvent and a transition state interact as the reaction occurs.

5.5 EFFECTS OF SOLVENT COHESION ENERGY ON RATES

If the behavior of a reaction is considered in terms of the volume change, the formation of the transition state can be viewed as the formation of a state having a different volume than that of the reactants. The change in volume can be written as

$$\Delta V^{\ddagger} = V^{\ddagger} - V_R \tag{5.69}$$

where V_R is the volume of the reactants and $V^{\ddagger}$ is the volume of the transition state. It is important to note that the *internal* pressure caused by the cohesion of the liquid results in an effect that is analogous to that produced by an *external* pressure (see Section 3.6). Accordingly, if the volume of activation is negative, the formation of the transition state will be enhanced when the solvent has a high internal pressure. Conversely, if the reaction has a positive volume of activation, the reaction will proceed faster in solvents having low internal pressure.

The effects of cohesion energy density or solubility parameter (δ) can be explained by considering a model in which cavities in the solution are altered as the reaction takes place. Cavity formation is hindered in solvents having large δ values. Moreover, the species having smaller volume (either the reactants or the transition state) will be favored in such solvents. If the reactants exist in cavities having a larger total volume than that of the transition state, a solvent of high cohesion energy will favor the formation of the transition state. These effects can be viewed in terms of a Boltzmann population of states having different energies with the energies of the states being altered by the solvent.

In terms of an overall chemical reaction, the cohesion energy density can often be used as a predictor of solvent effects on the rate. If the products have greater cohesion energy density than the reactants, the process will be favored when the solvent has a larger value for δ. Conversely, if the reactants have high cohesion energy density, a solvent having a large δ value retards the reaction. Predictably, if the reactants and products have similar cohesion energy densities, the δ value of the solvent will be relatively unimportant in its influence on the reaction. The cavities in a solution depend on the sizes of the species and the ability of the solvent to "compress" the cavity. Actually, if the solvent molecules are spherical, there will be free space in the pure solvent. We can see an analogy by considering a body-centered cubic structure similar to that found in solids. If a sphere is surrounded by eight others in a body-centered arrangement, it is easy to show there is 32% free space in the structure. When the interactions are of the "strong" dipole-dipole or hydrogen-bonding type, a solvent having a large δ value causes greater compression of the free space. Compression of this type is known as *electrostriction* of the free space. The effects of using solvents having different solubility parameters on reaction rates will be explored in more detail in Section 5.10.

5.6 SOLVATION AND ITS EFFECTS ON RATES

The complexity of reactions in solution has already been described briefly. However, many unimolecular reactions have rates in solutions that are approximately equal to those in the gas phase. The population of the transition state depends on the number of critical vibrational states populated, which is a function of temperature rather than the environment of the reacting molecule. The localization of the required energy in a vibrational mode for a bond to be broken is often somewhat independent of the environment of the molecule.

Generally, reacting molecules must come together and collide, form a transition state and react, and allow the products to be removed by diffusion from the reaction zone. In viscous media, the collision frequency of the reactants may limit the rate of formation of the transition state as a result of slow diffusion.

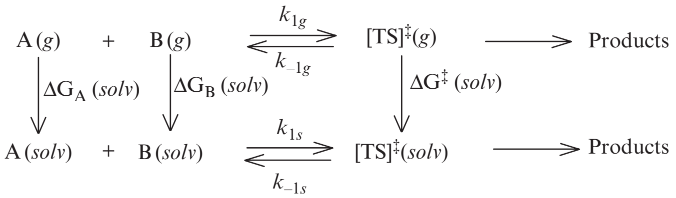
Consider a process in which two solvated reactant molecules A and B must come together to form a transition state. This process can be considered as requiring close proximity of A and B (sometimes called a *collision complex*) followed by the formation of the actual critical configuration in space, which is the reactive transition state. This process can be shown as follows.

$$\mathrm{A}(solv) + \mathrm{B}(solv) \xrightarrow{k_c} \mathrm{AB}(solv) \xrightarrow{k_a} [\mathrm{TS}]^{\ddagger}\ (solv) \qquad (5.70)$$

In this scheme, AB(*solv*) is the solvated collision complex of A and B, while $[\mathrm{TS}]^{\ddagger}(solv)$ is the solvated transition state. We can characterize the rate of formation of the collision complex by the rate constant k_c and that of the formation of the transition state by k_a. The rate of diffusion of A and B in the solution determines k_c, and there is an activation energy associated with that process. In an approximate way, the activation energy for diffusion can be considered as having a lower limit that is on the order of the activation energy for viscous flow of the solvent. Such energies are generally lower than those required to form transition states during chemical reactions. Therefore, $k_c >> k_a$, and the formation of the transition state is the rate-determining process. In the case of very viscous solvents and strong solvation of reactants A and B, the formation of the collision complex of A and B may be the rate-determining factor. In this case, the rate of the reaction is limited by the rate of formation of the collision complex, and the reaction is said to be *diffusion controlled*.

Although diffusion controlled reactions constitute a difficult special case, a general comparison of the behavior of gas phase reactions with those taking place in solution needs to be made. A problem with doing this is that few reactions that occur in the gas phase can be studied in solution under conditions that are otherwise the same with respect to temperature, concentration, etc. In some cases, even the products of the reaction may be different. The majority of studies on solvent effects have dealt with investigating the differences in kinetics of a reaction when different solvents are used rather than comparing the rates of gas phase reactions with those taking place in a solvent.

Let us consider the reaction between A and B that takes place in the gas phase and in some solvent to form the same products. We will write the process in the two phases as follows.



If the transition states formed under the two sets of conditions are identical except for solvation and have equal probabilities for reaction, the rate of the reaction in each case will be determined only by the concentration of the transition state. Therefore,

$$\text{Rate} \sim [\text{TS}]^{\ddagger} \tag{5.71}$$

For the reaction in the gas phase,

$$\text{R}_g \sim [\text{TS}]_g^{\ddagger} = \text{K}_g^{\ddagger}[\text{A}]_g[\text{B}]_g \tag{5.72}$$

and for the reaction in solution,

$$\text{R}_s \sim [\text{TS}]_s^{\ddagger} = \text{K}_s^{\ddagger}[\text{A}]_s[\text{B}]_s \tag{5.73}$$

where $\text{K}_g^{\ddagger}$ and $\text{K}_s^{\ddagger}$ are the equilibrium constants for the formation of the transition states in the gas phase and in solution. Therefore, when the concentrations of A and B are identical in the two phases, the ratio of the rates is given by the ratio of the equilibrium constants,

$$\frac{\text{R}_g}{\text{R}_s} = \frac{\text{K}_g^{\ddagger}}{\text{K}_s^{\ddagger}} \tag{5.74}$$

The equilibrium constants for the formation of the transition states in the two phases can be written in terms of the rate constants as

$$K_g^{\ddagger} = \frac{k_{1g}}{k_{-1g}} \text{ and } K_s^{\ddagger} = \frac{k_{1s}}{k_{-1s}} \tag{5.75}$$

Consequently, making use of the principles illustrated in Chapter 2, we obtain

$$\frac{R_g}{R_s} = \frac{K_g^{\ddagger}}{K_s^{\ddagger}} = \frac{e^{-\Delta G_g^{\ddagger}/RT}}{e^{-\Delta G_s^{\ddagger}/RT}} \tag{5.76}$$

This equation can be written in logarithmic form as

$$\ln \frac{R_g}{R_s} = \frac{\Delta G_s^{\ddagger} - \Delta G_g^{\ddagger}}{RT} \tag{5.77}$$

This equation shows that the difference in free energy of activation in the gas phase and in the solvent determines any difference in reaction rate. We can also write Eq. (5.76) in terms of the enthalpy and entropy of activation as

$$\frac{R_g}{R_s} = \frac{e^{\Delta S_g^{\ddagger}/R} e^{-\Delta H_g^{\ddagger}/RT}}{e^{\Delta S_s^{\ddagger}/R} e^{-\Delta H_s^{\ddagger}/RT}} \tag{5.78}$$

which can be simplified to give

$$\frac{R_g}{R_s} = e^{(\Delta S_g^{\ddagger} - \Delta S_s^{\ddagger})/R}\ e^{(\Delta H_s^{\ddagger} - \Delta H_g^{\ddagger})/RT} \tag{5.79}$$

It is readily apparent that when solvation effects on forming the transition state in solution are negligible compared to those on forming the transition state in the gas phase, $\Delta S_g^{\ddagger} = \Delta S_s^{\ddagger}$ and $\Delta H_g^{\ddagger} = \Delta H_s^{\ddagger}$, so $R_g = R_s$ and the rate of the reaction will be the same in the gas phase and in solution.

In a general way, we can see the effect of the choice of solvent on a reaction by considering the free energy of activation. Figure 5.3 shows the cases that might be expected to arise when a reaction is studied in the gas phase and in four different solvents. In solvent 1, the reactants are strongly solvated so they reside at a lower free energy than they do in the gas phase. However, in this case the solvent is one that strongly solvates the transition state so it too resides at a lower free energy in the solvent than it does in the gas phase, and by a greater amount than do the reactants. Therefore, solvent

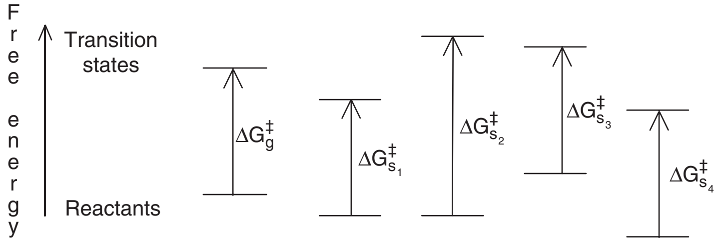


FIGURE 5.3 Effects of solvation of reactants and transition states on the free energy of activation. See text for explanation of the various cases. Subscripts indicate gas and solvents 1, 2, 3, and 4.

1 will increase the rate of reaction relative to that of the gas phase reaction because $\Delta G^{\ddagger}_{s1} < \Delta G^{\ddagger}_{g}$.

In solvent 2, solvation of the reactants leads to the reactants residing at a lower free energy, but the transition state is not solvated strongly and is destabilized compared to the gas phase transition state. Therefore, $\Delta G^{\ddagger}_{s2} > \Delta G^{\ddagger}_{g}$ and the reaction will proceed at a lower rate than it will in the gas phase. In solvent 3, neither the reactants nor the transition state is well solvated. In this case, the reactants and the transition state have higher free energies than they do for the gas phase reaction, but $\Delta G^{\ddagger}$ is unchanged. Therefore, the reaction should take place at about the same rate in solvent 3 as it does in the gas phase. Finally, in solvent 4, a solvent that strongly solvates both the transition state and the reactants, the rate should also be about the same as it is in the gas phase because $\Delta G^{\ddagger}_{s4} \approx \Delta G^{\ddagger}_{g}$.

The foregoing discussion is based on the effects of solvation of reactants and transition states on $\Delta G^{\ddagger}$. However, because of the relationship

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{5.80}$$

it is apparent that an effect on $\Delta G^{\ddagger}$ could arise from a change in $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ (assuming that they do not change in a compensating manner as described in Section 5.9). For example, when the reactions

$$CH_3Cl + N_3^- \rightarrow CH_3N_3 + Cl^- \tag{5.81}$$

$$i\text{–}C_4H_9Br + N_3^- \rightarrow i\text{–}C_4H_9N_3 + Br^- \tag{5.82}$$

were studied by Alexander and coworkers (1968) in methanol and DMF ($HCON(CH_3)_2$), the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were found to reflect the difference in the influence of the solvent. For these reactions, $\Delta H_M{}^{\ddagger}$ and $\Delta S_M{}^{\ddagger}$ are the activation parameters in methanol and $\Delta H_{DMF}{}^{\ddagger}$ and $\Delta S_{DMF}{}^{\ddagger}$ are the same parameters in DMF.

When $(\Delta H_M{}^{\ddagger} - \Delta H_{DMF}{}^{\ddagger})/2.303RT$ and $(\Delta S_M{}^{\ddagger} - \Delta S_{DMF}{}^{\ddagger})/R$ are compared for the reaction shown in Eq. (5.82) at 25°C, the values are 4.3 and 1.0, respectively. The value of $\Delta H_M{}^{\ddagger} - \Delta H_{DMF}{}^{\ddagger}$ being positive indicates that formation of the transition state is more difficult in methanol than it is when the solvent is DMF. When expressed in the conventional way, $\Delta H_M{}^{\ddagger} - \Delta H_{DMF}{}^{\ddagger} = 24.5$ kJ/mol, while $\Delta S_M{}^{\ddagger} - \Delta S_{DMF}{}^{\ddagger} = 19$ J/mol (which is 0.019 kJ/mol). It is apparent that the effect of changing solvents is due predominantly to the effect on $\Delta H^{\ddagger}$ and that entropy differences are only minor.

The origin of the solvent effect just described has been explored in the following way. The enthalpies of transfer (the difference in the heats of solution), ΔH_{tr}, of $(C_2H_5)_4NX$ (X = Cl, Br, or I) from water to dimethyl sulfoxide (DMSO) were determined, and they were expressed relative to the value for the iodide compound. The free energies associated with changing solvents, ΔG_{tr}, of the corresponding silver compounds were measured and expressed relative to AgI. By comparison of the values of ΔH_{tr} for the $(C_2H_5)_4NX$ compounds with the ΔG_{tr} values for the AgX compounds, the effects of cation cancel, so the differences in ΔG_{tr} and ΔH_{tr} can be compared. The results given by Parker and coworkers (1968) are as follows for the anions listed (given as the anion: ΔG_{tr} (kJ/mol): ΔH_{tr} (kJ/mol)): Cl^- : 29 : 31; Br^- : 16 : 16; I^-: 0: 0 (the reference). The fact that $\Delta H_{tr} \approx \Delta G_{tr}$ indicates that the entropy effects caused by changing solvent are negligible. Further, it is clear that the differences in behavior of ΔG_{tr} when changing solvents are primarily due, at least for Cl^-, Br^-, and I^-, to differences in solvation enthalpies. In the case of these ions, the trend in solvation enthalpies from H_2O to DMSO is what would be expected because Cl^- is a rather small and hard species, and it is more strongly solvated in water, so ΔH_{tr} is more positive when Cl^- is transferred to DMSO. The bromide ion, being large and softer, is not much more strongly solvated by water than it is by DMSO. One could also expect that I^- might be about equally well solvated by the two solvents.

When a transition state is formed from a reactant molecule, the electrostatic charge distribution is changed. As a result, solvation factors are not static. A reactant may become a better electron donor or acceptor as the transition state forms, which may result in increased or decreased interactions with the solvent. Consequently, Hammet σ constants that are obtained in one type of solvent (say a protic, polar solvent such as CH_3OH) may not apply quantitatively in a solvent such as DMSO or CH_3CN (see Section 5.8).

5.7 EFFECTS OF IONIC STRENGTH

When ions react in solution, their charges result in electrostatic forces that affect the kinetics of the reactions. We can see how this situation arises in the following way. If a reaction occurs between a cation having a charge Z_A and an anion having a charge of Z_B, the transition state will be $[AB]^{ZA+ZB}$. The equilibrium constant for the formation of the transition state can be written in terms of the activities of the species as

$$K^{\ddagger} = \frac{a^{\ddagger}}{a_A a_B} = \frac{[TS]^{\ddagger}\gamma_{\ddagger}}{[A]\gamma_A[B]\gamma_B} \tag{5.83}$$

where a is an activity and γ is an activity coefficient. From this equation, we obtain

$$[TS]^{\ddagger} = \frac{K^{\ddagger}\gamma_A\gamma_B[A][B]}{\gamma_{\ddagger}} \tag{5.84}$$

For the reaction A $\rightarrow$ B, the rate of the reaction can be written as

$$-\frac{d[A]}{dt} = k[TS]^{\ddagger} = kK^{\ddagger}[A][B]\frac{\gamma_A\gamma_B}{\gamma_{\ddagger}} \tag{5.85}$$

When written in terms of the frequency of the decomposition of the transition state, ν, which is equal to $\mathbf{k}T/h$, the rate equation becomes

$$-\frac{d[A]}{dt} = \frac{\mathbf{k}T}{h}\cdot\frac{\gamma_A\gamma_B}{\gamma_{\ddagger}} \tag{5.86}$$

If the solution is sufficiently dilute so that the Debye-Hückel limiting law applies,

$$\log\gamma_i = -0.509Z_i^2 I^{1/2} \tag{5.87}$$

where Z_i is the charge on the species and I is the ionic strength of the solution. Therefore,

$$\log k = \log\frac{\mathbf{k}T}{h}K^{\ddagger} + \log\frac{\gamma_A\gamma_B}{\gamma_{\ddagger}} \tag{5.88}$$

which by expanding the term containing the activity coefficients can be written as

$$\log k = \log\frac{\mathbf{k}T}{h}K^{\ddagger} + \log\gamma_A + \log\gamma_B - \log\gamma_{\ddagger} \tag{5.89}$$

Substituting for the terms containing log γ gives

$$\log k = \log\frac{\mathbf{k}T}{h}K^{\ddagger} - 0.509(Z_A^2 + Z_B^2 - Z_{\ddagger}^2)I^{1/2} \tag{5.90}$$

The charge on the transition state $[TS]^{\ddagger}$ is $Z_A + Z_B$, so

$$Z_{\ddagger}^2 = (Z_A + Z_B)^2 = Z_A^2 + Z_B^2 + 2Z_AZ_B \tag{5.91}$$

Therefore, when this result is substituted in Eq. (5.90), after simplification we obtain

$$\log k = \log\frac{\mathbf{k}T}{h}K^{\ddagger} + 1.018Z_AZ_BI^{1/2} \tag{5.92}$$

When the first term on the right-hand side of this equation is represented as k_o, this equation can be written in logarithmic form as

$$\log\frac{k}{k_o} = 1.018Z_AZ_BI^{1/2} \tag{5.93}$$

At constant temperature, the first term on the right-hand side of Eq. (5.92) is a constant, so it is apparent that a plot of log k versus $I^{1/2}$ should be linear. If at least one reactant is not a charged species, Z_A or Z_B will be zero, and the ionic strength of the reaction medium should have little or no effect on the rate of the reaction. However, if A and B are both positive or both negative, the rate of the reaction should increase linearly with $I^{1/2}$. If A and B are oppositely charged, the rate of the reaction should decrease linearly with $I^{1/2}$. In these cases, the slope of the plot of log k versus $I^{1/2}$ is directly proportional to the magnitude of Z_AZ_B. Observations on many reactions carried out in dilute solutions are in accord with these predictions. Figure 5.4 shows the expected variation in rate constant as ionic strength of the solution varies.

The explanation for the observations when the product Z_AZ_B is positive lies in the fact that when the ionic strength is *high*, the solvated ions change the dielectric behavior of the solution so that ions of like charge do not repel each other as greatly. This allows them to approach more closely, which causes an increase in collision frequency and an *increased* reaction rate. When the ions are of *opposite* charge, an increase in the concentration of ions in the solvent causes a decrease in the attraction between the ions so that the rate of the reaction between them is *decreased*. Deviations from predicted behavior are common even when the solutions are quite dilute because the Debye-Hückel limiting law applies only to very dilute

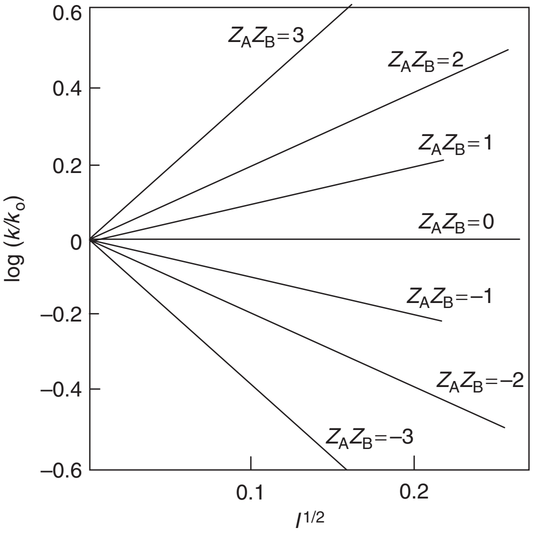


FIGURE 5.4 The effect of ionic strength on the rates of reactions between ions as a function of ionic strength of the solution (k_o is the rate constant at $I = 0$).

solutions. It should also be mentioned that ion pairing and complex formation can cause the relationship to be far from exact.

For reactions that involve uncharged reactants, the ionic strength of the solution should be expected to have little effect on the reaction rate. If the reaction is one in which ions are consumed or generated, the overall ionic strength of the medium will change as the reaction progresses. Such a situation will alter the kinetic course of the reaction. In order to avoid this situation, one of two approaches must be used. First, the change in ionic strength that occurs during the reaction can be determined and the results can be adjusted to compensate for the change. A more common approach is to carry out the reaction at a relatively high and essentially constant ionic strength by preparing a reaction medium that contains a large concentration of an "inert" salt to provide "ionic ballast." For many substitution reactions, the choice of salt is relatively easy since ions like ClO_4^-, NO_3^-, BF_4^-, or PF_6^- are not good nucleophiles and do not compete with most entering groups. If the reaction is one in which the electrophilic character of the cation is important, salts such as $R_4N^+Cl^-$ may be used because tetraalkylammonium ions are not electrophiles. Obviously, some discretion must be exercised in the choice of "inert" salt in light of the reaction being studied. A realistic approach is to carry out the reaction by

making duplicate runs with different salts present at identical concentrations. If the rate of the reaction is the same in both cases, the salt being tested is actually inert.

5.8 LINEAR FREE ENERGY RELATIONSHIPS

The term *linear free energy relationship* (LFER) applies to a variety of relationships between kinetic and thermodynamic quantities that are important in both organic and inorganic reactions. About 80 years ago, J. N. Brønsted found a relationship between the dissociation constant of an acid, K_a, and its ability to function as a catalyst in reactions that have rates that are accelerated by an acid. The Brønsted relationship can be written in the form

$$k = CK_a{}^n \tag{5.94}$$

where k is the rate constant, K_a is the dissociation constant for the acid, and C and n are constants. Taking the logarithm of both sides of this equation gives

$$\ln k = n \ln K_a + \ln C \tag{5.95}$$

or when common logarithms are used,

$$\log k = n \log K_a + \log C \tag{5.96}$$

Recalling the definition

$$pK_a = -\log K_a \tag{5.97}$$

allows Eq. (5.95) to be written as

$$\log k = -n \ pK_a + \log C \tag{5.98}$$

From this equation, we can see that a plot of log k versus pK_a should be linear. However, the anion, A^-, of the acid HA is capable of functioning as a base that reacts with water.

$$A^- + H_2O \rightleftharpoons HA + OH^- \tag{5.99}$$

Therefore, we can write the equilibrium constant for this reaction, K_b, as

$$K_b = \frac{[HA][OH^-]}{[A^-]} \tag{5.100}$$

Some reactions are catalyzed by bases so we can obtain relationships that are analogous to Eqs. (5.95) and (5.96), and the first is written as

$$\log k' = n' \log \mathrm{K_b} + \log C' \tag{5.101}$$

In aqueous solutions, $\mathrm{K_b}$ can be written as $\mathrm{K_w/K_a}$ where $\mathrm{K_w}$ is the ion product constant for water. Therefore, Eq. (5.101) can also be written as

$$\log k' = n' \log\left(\frac{\mathrm{K_w}}{\mathrm{K_a}}\right) + \log C' \tag{5.102}$$

In base catalysis, the rate of the reaction is directly dependent on the strength of the base, but it is inversely related to the strength of the conjugate acid.

Because the equilibrium constant for dissociation of an acid is related to the free energy change by

$$\Delta \mathrm{G_a} = -\mathrm{RT} \ln \mathrm{K_a} \tag{5.103}$$

substitution for $\ln \mathrm{K_a}$ in Eq. (5.96) leads to

$$\ln k = -\frac{n\Delta \mathrm{G_a}}{\mathrm{RT}} + \ln C \tag{5.104}$$

This equation shows that a linear relationship should exist between ln k for the acid catalyzed reaction and $\Delta \mathrm{G_a}$ for dissociation of the acid. This is an example of a linear free energy relationship.

When two similar acids are considered, the rate constants for reactions in which they are catalysts will be given by k_1 and k_2, while the dissociation constants will be given by $\mathrm{K_{a1}}$ and $\mathrm{K_{a2}}$. Then, subtracting the equation relating k and $\mathrm{K_a}$ for the second acid from that for the first acid yields the equation

$$\ln k_1 - \ln k_2 = n(\ln \mathrm{K_{a1}} - \ln \mathrm{K_{a2}}) \tag{5.105}$$

This equation can be rearranged to give

$$\ln \frac{k_1}{k_2} = n \ln \frac{\mathrm{K_{a1}}}{\mathrm{K_{a2}}} = nm \tag{5.106}$$

where m is a constant that is equal to the logarithm of the ratio of the dissociation constants for the two acids. As we shall see, when common logarithms are used and the constants on the right-hand side of the equation are represented as ρ and σ, the relationship is known as the *Hammett equation*,

$$\log \frac{k}{k_o} = \rho\sigma \tag{5.107}$$

where k_o is the rate constant for the reaction in the presence of the reference acid. Numerous special cases of this type of equation exist where closely similar reactions are compared to a reference reaction. For example, the rates of hydrolysis of alkyl halides have been correlated in this way.

The Hammett LFER relates the dissociation constants of substituted benzoic acids to that of benzoic acid itself. Described in 1937, the original relationship was developed to explain the electronic effects of substituents on the strengths of *m*- and *p*-substituted benzoic acids. Then, the parameter σ was defined for *m*- and *p*-substituted acids as

$$\sigma_m = \log \frac{K_{mx}}{K_o} \tag{5.108}$$

$$\sigma_p = \log \frac{K_{px}}{K_o} \tag{5.109}$$

where K_o is the dissociation of benzoic acid (the reference) and K_{mx} and K_{px} are the dissociation constants of the *m*- and *p*-XC_6H_4COOH acids that have a group X in the *m* and *p* positions. If the group X is electron withdrawing, the acidity of the COOH group is increased and σ is positive. Conversely, the σ values are negative for electron releasing groups. When the dissociation constants for the acids XC_6H_4COOH were studied, a linear relationship between $\log(K'_x/K'_o)$ (where K'_o is the dissociation constant for the reference acid, $C_6H_5CH_2COOH$) and the σ values was obtained. Unlike the equations given earlier where the slope is unity, the constant slope was represented as ρ so that

$$\log \frac{K'_x}{K'_o} = \rho\sigma \tag{5.110}$$

When a series of reactions is studied in which the strength of the acid is a rate-determining factor, the rates will be proportional to $[H^+]$, but this is in turn proportional to K_a. Therefore, the rate constants will be related by the equation

$$\log \frac{k_x}{k_o} = \rho\sigma \tag{5.111}$$

When other series of aromatic compounds are considered, the constants K_o and k_o refer to the reference unsubstituted acid. Equation (5.111) shows that if $\rho > 1$, the rate or dissociation constant is enhanced by the electronic effects of substituent X to a greater extent than they are for the benzoic

acids. On the other hand, if $\rho < 0$, the group X is electron releasing and the rate (or dissociation) constant is increased by the presence of group X. Finally, if $1 > \rho > 0$, the rate (or dissociation) constant is increased, but to a lesser extent than the benzoic acid is affected by the same substituent. While the major use of the Hammett relationship is in organic chemistry, a number of interesting correlations have been found for some inorganic reactions involving complexes as well.

The relationship

$$\log\frac{K_x}{K_o} = \rho\sigma \tag{5.112}$$

can be written as

$$\log K_x - \log K_o = \rho\sigma \tag{5.113}$$

and because

$$\Delta G = -RT \ln K = -2.303\, RT \log K \tag{5.114}$$

we find that

$$\log K = -\frac{\Delta G}{2.303RT} \tag{5.115}$$

Therefore, for a reference acid that has a dissociation constant K_o and another acid that has a dissociation constant K_x,

$$\log K_x - \log K_o = \rho\sigma \tag{5.116}$$

and by substitution, we obtain

$$-\frac{\Delta G_x}{2.303RT} + \frac{\Delta G_o}{2.303RT} = \rho\sigma \tag{5.117}$$

which can be simplified to give

$$\Delta G_x = \Delta G_o - 2.303\ RT\ \rho\sigma = \Delta G_o - (\text{constant})\ \rho\sigma \tag{5.118}$$

This equation shows the *linear* relationship between the change in free energy and the product of $\rho\sigma$.

The LFER of Hammett is satisfactory only when the reactive site is sufficiently removed from the substituent so that steric factors do not enter into the rate-determining step of the reaction. Also, if the reaction involves a series of substituents that greatly alter the way in which either the reactant or the transition state is solvated, the relationship may be less than satisfactory. It is perhaps wise to remember that the relationships are empirical in origin. This does not detract from their usefulness, neither is it any different

for empirically determined rate laws. While the original Hammett LFER was applied to aromatic compounds, other studies have extended it to other types of compounds (e.g., aliphatic).

The approach taken by R. W. Taft is similar to that of Hammett, and the equation used can be written as

$$\log\frac{k}{k_o} = \rho^*\sigma^* + \delta E_s \tag{5.119}$$

where σ^* is a constant related to polar substituent effects and ρ^*, as was the case for ρ, is a reactant constant, and δE_s is a steric energy term. When a given series of reactants is considered, δE_s is frequently considered to be zero since for any pair of similar species subtraction of two equations having the form of (5.119) would cause the term δE_s to cancel. Frequently, the *Taft equation* is written simply as

$$\log\frac{k}{k_o} = \rho^*\sigma^* \tag{5.120}$$

The Taft equation is essentially similar to the Hammett relationship but has constants that are also appropriate to aliphatic and restricted aromatic materials.

5.9 THE COMPENSATION EFFECT

When a series of reactions involving similar reactants (e.g., a series of substituted molecules having different substituents in a particular position) is studied, it is possible to find that $\Delta G^\ddagger$ may show little variation for the series. This may be indicative of there being a relationship of the Hammett or Taft type. However, another explanation that is appropriate in some cases is the so-called *compensation effect.*

We can see how this situation might arise in a very simple way. As an extreme example, consider the solvation of the ions that are present in reactions as the transition states TS_1 and TS_2. Suppose one has a charge of $+TS_1$ and the other has a charge that is $+TS_2$, where $TS_2 > TS_1$. In a polar solvent, TS_2 will be more strongly solvated than TS_1, so $\Delta H_2^\ddagger$ will be more negative than $\Delta H_1^\ddagger$. However, because this is true, the solvent in the vicinity of TS_2 will be more ordered than it is near TS_1, and $\Delta S_2^\ddagger$ will be more negative than $\Delta S_1^\ddagger$. The free energy of activation, $\Delta G^\ddagger$, is given by

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \tag{5.121}$$

Therefore, if $\Delta H_2^\ddagger$ is more negative than $\Delta H_1^\ddagger$ and $\Delta S_2^\ddagger$ is more negative than $\Delta S_1^\ddagger$, it is possible that $\Delta G^\ddagger$ may be approximately constant for the two cases. For a series of reactions, we might find that

$$\Delta H_1^\ddagger - T\Delta S_1^\ddagger = C \tag{5.122}$$

where C is a constant. Therefore, we can write

$$\Delta H_1^\ddagger = T\Delta S_1^\ddagger + C \tag{5.123}$$

and we should expect that a plot of $\Delta H^\ddagger$ versus $\Delta S^\ddagger$ should be linear with a slope of T. This temperature is sometimes called the *isokinetic temperature* in this *isokinetic relationship*. Figure 5.5 shows such a relationship for the reaction

$$[Cr(H_2O)_5OH]^{2+} + X^- \rightarrow [Cr(H_2O)_5X]^{2+} + OH^- \tag{5.124}$$

where X = Cl^-, Br^-, I^-, SCN^-, etc. In this case, a reasonably good linear relationship results when the graph is made in spite of the fact that widely different entering ligands were used. The mechanism of these substitution reactions involves the initial loss of OH^- followed by the entry of X^- into the coordination sphere.

Although we have interpreted the compensation effect in terms of transition states having different charges, there is no reason that transition states having different polarities could not behave similarly when the solvent is polar. Also, if a reduction in charge separation occurs as the transition state forms and the solvent is nonpolar, more favorable solvation

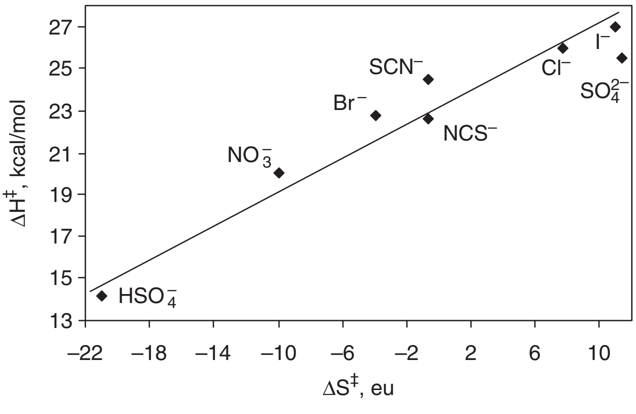


FIGURE 5.5 An isokinetic plot for the formation of $[Cr(H_2O)_5X]^{2+}$ by replacement of OH^-. (Constructed from the data given in D. Thusius, *Inorg. Chem.*, 1971, *10*, 1106.)

of the transition state would be expected on the basis of the hard-soft interaction principle. A compensation effect could result in this situation also. When a linear isokinetic relationship is obtained, it is usually taken as evidence for a common mechanism for the series of reactions.

5.10 SOME CORRELATIONS OF RATES WITH SOLUBILITY PARAMETER

The importance of solvent cohesion energy, as reflected by the solubility parameter, and its usefulness for interpreting the effect of the solvent were described briefly in Section 5.5. Because the solubility parameter is such an important (and underutilized) tool for explaining solvent effects on rates, we will describe here more of the details of a few studies. In a general way, solvents having large solubility parameters assist the formation of transition states in which there is high polarity or charge separation (high cohesion energy in the transition state). Conversely, solvents that have large, non-polar structures hinder the formation of transition states that have large, nonpolar structures.

A reaction that is widely cited as one in which solvent *polarity* plays a major role is the formation of quaternary ammonium salts as shown in the equation

$$R_3N + R'X \rightarrow R'R_3N^+X^- \qquad (5.125)$$

However, the effect of a series of solvents can also be interpreted in terms of the solubility parameters of the solvents. The transition state in this reaction is generally regarded as resembling the product (meaning that it has considerable charge separation and high cohesion energy). Accordingly, it would be logical to expect that the rate of the reaction would be enhanced by using solvents having large solubility parameters. One such reaction of this type that has been studied by Kondo, et al. (1972) in a variety of solvents is

$$C_6H_5CH_2Br + C_5H_5N \rightarrow C_5H_5NCH_2C_6H_5^+Br^- \qquad (5.126)$$

For this reaction, it was found that the rate increases when solvents having large solubility parameters are used. Moreover, the volume of activation for the reaction is negative in all of the solvents, but it is more negative in solvents having smaller solubility parameters.

The free energy of activation for a reaction having a compact, polar (or ionic) transition state will be decreased by solvents having large solubility

parameters. The equilibrium constant for the formation of the transition state is

$$K^{\ddagger} = \frac{k_1}{k_{-1}} \tag{5.127}$$

where k_1 is the rate constant for the formation of the transition state and k_{-1} is the rate constant for its decomposition. The free energy of activation is related to $K^{\ddagger}$ by the relationship

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{5.128}$$

Because the rate of the reaction will be proportional to the concentration of the transition state, which is in turn related to $K^{\ddagger}$, we would expect that a plot of ln k versus solubility parameter would be linear. We are assuming in this case that the decrease in the free energy of activation is directly proportional to the ability of the solvent to "force" the formation of the transition state. Figure 5.6 shows a test of this relationship using the data given by Kondo, et al. (1972) for the reaction of benzylbromide with pyridine, which is the represented by Eq. (5.126). It can be seen that for most of the solvents the relationship is approximately correct.

Furthermore, the ability of the solvent to solvate a transition state that has charge separation is related to the solubility parameter of the solvent. As shown in Figure 5.7, the majority of the solvents give a satisfactory relationship between $\Delta V^{\ddagger}$ and δ in spite of the fact that widely differing solvents were used.

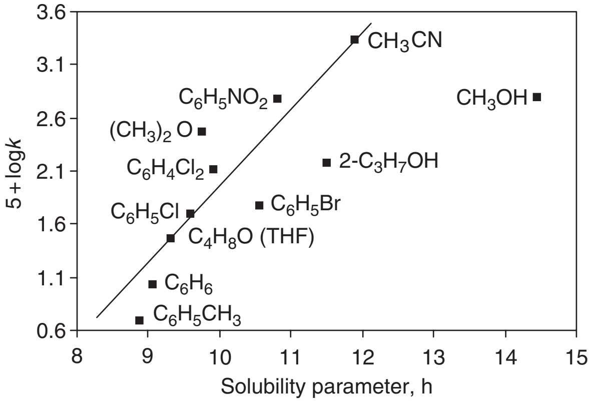


FIGURE 5.6 Relationship between the rate constants for the reaction shown in Eq. (5.126) and the solubility parameter of the solvent. (Constructed using the data of Kondo, et al. (1972).)

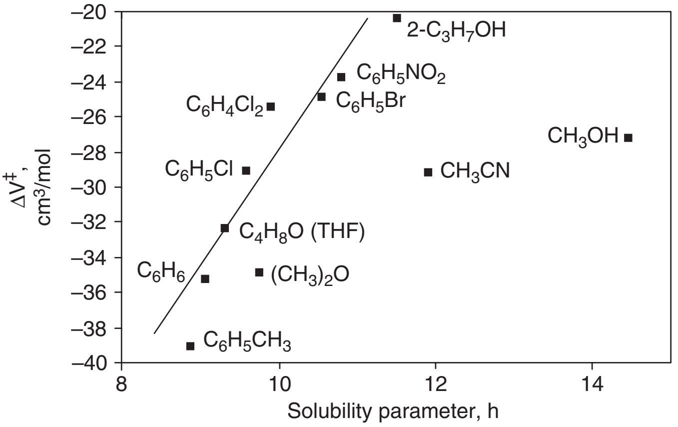


FIGURE 5.7 Relationship between the volume of activation for the reaction shown in Eq. (5.126) and the solubility parameter of the solvent. (Constructed using the data of Kondo, et al. (1972).)

However, two liquids, CH_3CN and CH_3OH, give data that fall far from the line. The solubility parameters for these liquids are larger because of strong dipole-dipole forces (in CH_3CN) and hydrogen bonding (in CH_3OH). The fact that the volume of activation is more negative for solvents with lower cohesion energies is a reflection of the fact that these liquids have more loosely packed structures and that the reactants are much less constricted in these solvents than they are in the transition state. If the transition state is approximately the same in volume when different solvents are used, the *reactants* must occupy a larger effective volume in the solvents of lower solubility parameter. The fact that the solvents CH_3CN and CH_3OH result in an abnormal volume of activation is probably due to the fact that these solvents have much more structure and the reactants already exist in small cavities as a result of electrostriction of the solvent. These solvents are less compressible and have already become tightly bound around the solutes. Consequently, there is a smaller volume change when the transition state forms when the solvent is CH_3OH or CH_3CN.

We can examine the relationship between the solubility parameter of the solvent and the rate of a similar reaction by making use of the data given by Laidler (1965, p. 203) for the reaction

$$(C_2H_5)_3N + C_2H_5I \rightarrow (C_2H_5)_4N^+I^- \qquad (5.129)$$

Figure 5.8 shows a plot of log k versus δ for this reaction carried out at 100°C.

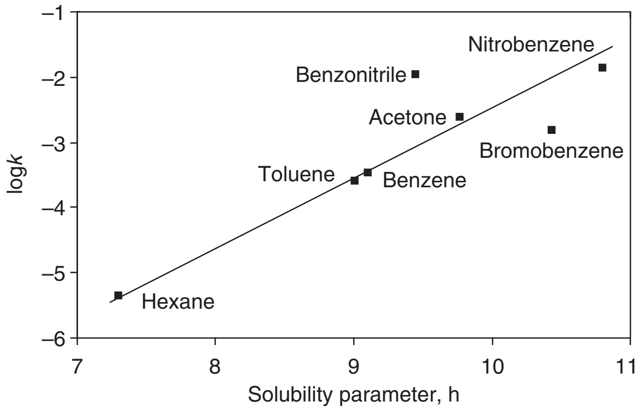


FIGURE 5.8 Relationship between the rate constants for the reaction between ethyl iodide and triethylamine and the solubility parameters of the solvents. (Constructed using the rate constants given by Laidler (1965).)

It is clear that the relationship is approximately linear, and as expected, the rate of the reaction increases with increasing solubility parameter of the solvent. As a general rule, we can conclude that *reactions that pass through transition states that have considerable polarity (or charge separation) induced will have rates that increase with increasing solubility parameter of the solvent.*

We should ask at this point what happens when reactions of a totally different type take place in solvents having different solubility parameters. Reactions in which the transition state is a large, essentially nonpolar species behave in exactly the opposite way to those discussed earlier with respect to the effects of the solvent on the rate of reaction. One case of this type is the esterification that occurs when acetic anhydride reacts with ethanol at 50°C. Using the data given by Laidler (1965, p. 209), Figure 5.9 was constructed showing the relationship between log k and δ. For this reaction, the rate of the reaction is seen clearly to decrease as the solubility parameter of the solvent increases. The formation of a large transition state having little or no charge separation from two smaller, polar molecules is hampered by solvents having high cohesion energy (or δ). Accordingly, a linear relationship also exists between log k and δ, but the slope is negative in this case.

Parker and coworkers have investigated solvent effects on a variety of organic reactions. In one massive study on S_N2 reactions (Parker, et al., 1968), data are presented for a large number of substitution reactions carried out in a wide range of solvents. Data for two of the numerous

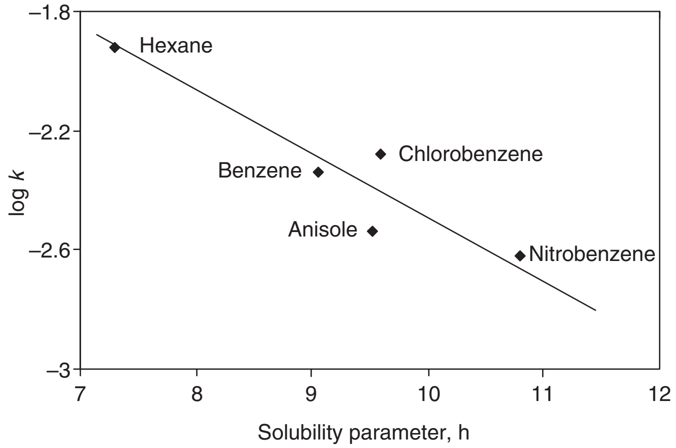


FIGURE 5.9 Dependence of the rate constants for the reaction between acetic anhydride and ethyl alcohol on the solubility parameters of the solvents. (Constructed using rate constants given by Laidler (1965).)

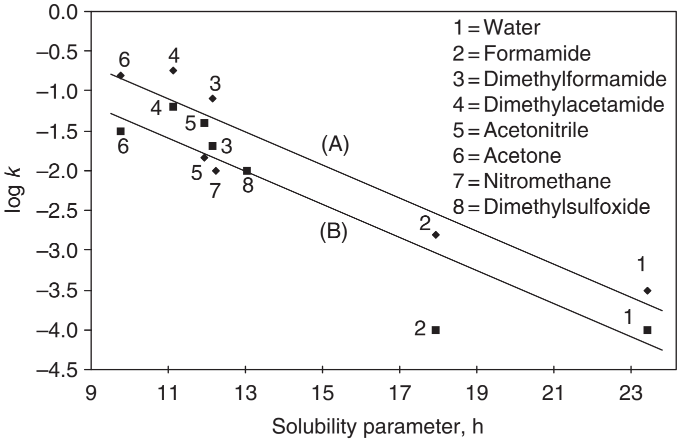


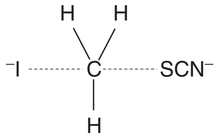
FIGURE 5.10 Relationship between log k and the solubility parameter of the solvent for nucleophilic substitution. (Constructed using the rate constants from Parker, et al. (1968).

reactions studied were used to construct Figure 5.10, which shows the variation in log k as a function of the solubility parameters of the solvents. It is readily apparent that for the reactions

$$CH_3I + SCN^- \rightarrow CH_3SCN + I^- \quad (5.130)$$

$$n\text{-}C_4H_9Br + N_3^- \rightarrow n\text{-}C_4H_9N_3 + Br^- \quad (5.131)$$

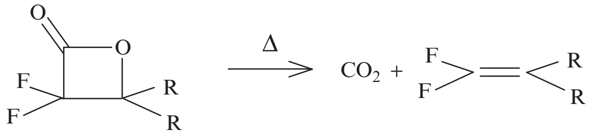
the rate of substitution decreases more or less linearly with increasing solubility parameter of the solvent. In the first of these reactions, SCN^- is more strongly solvated by solvents that contain small, protic molecules (e.g., water or formamide) than is I^-. If a transition state such as



is formed, the charge is dissipated over a large structure so solvents that consist of molecules that are essentially small and hard in character will not solvate the transition state as well as they will the SCN^-. On the other hand, solvents that are essentially soft in character (acetone, acetonitrile, or dimethyacetamide) will solvate the transition state more strongly than they will the reactants. As a result, the rate of the reaction will be greater in softer solvents than it will in solvents that consist of small, polar molecules (having larger δ values). Figure 5.10 shows that these conclusions are borne out by the data for the reaction shown in Eq. (5.130).

Although the rates are lower for the reaction shown in Eq. (5.131) than those for the reaction shown in Eq. (5.130) in each of the solvents tested, the same trend is seen for the reaction of *n*-butyl bromide with azide ion. The azide ion will be rather strongly solvated by solvents that consist of small, polar molecules while the bromide ion will be less well solvated by such solvents. Also, the transition state will have the charge spread over a larger volume so that solvents that are composed of soft molecules will solvate the transition state better than those that consist of small, polar molecules. These conclusions are in accord with the trends shown in Figure 5.10.

Another reaction in which the solvent plays an enormous role is in the decarboxylation of lactones. In one study of this type, Ocampo, Dolbier, Bartberger, and Paredes (1997) investigated the decarboxylation of α,α-difluoro β-lactones in several solvents and in the gas phase. The reaction for the dialkyl compounds can be shown as follows.



(5.132)

When the decarboxylation of the dimethyl compound was studied in the gas phase, the activation energy was found to be 189 kJ/mole. For the reaction

carried out in solutions, the activation energy ranged from 114–137 kJ/mol depending on the solvent. From this and other evidence it was concluded that the reaction follows a different pathway in the two phases. It was concluded that the gas phase reaction takes place by a concerted mechanism that involves a planar, homolytic nonpolar transition state. In polar solvents the reaction probably involves a zwitterion intermediate.

The rate constants for the reaction of the diethyl compound were determined in various solvents at a temperature of 168.1°C. A pathway involving charge separation was postulated for the reaction in solution, and the rate constants were correlated with a solvent parameter known as the E_T value. In view of the success of correlating rates in solution with the solubility parameter of the solvent, the log k values were plotted against δ to obtain the result shown in Figure 5.11.

The correlation of the rates of decarboxylation of the difluoro diethyl lactone with solubility parameter shows that the rate increases dramatically as the value of δ increases. In fact, there was a factor of almost 500 difference in the rate constants depending on the solvent chosen. This is in agreement with the conclusion that the transition state for the reaction carried out in solution involves a substantial separation of charge. Furthermore, Figure 5.11 shows that the solubility parameter can be a useful index for assessing the role of the solvent in a reaction of a greatly different type than those described earlier in this chapter. The entropy of activation for the reaction was reported

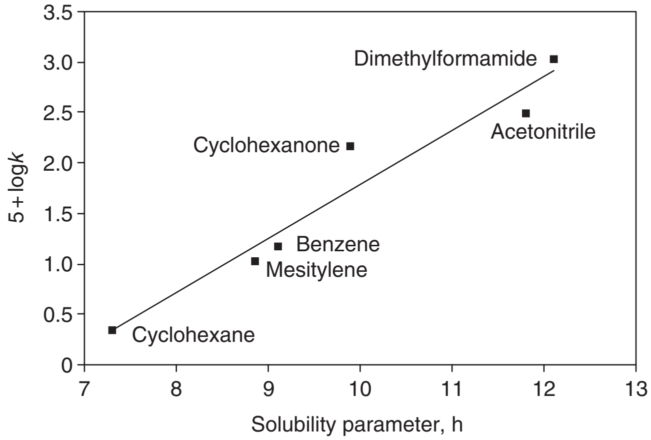


FIGURE 5.11 Correlation of rate constants for decarboxylation of 3,3–difluoro–4, 4–diethyloxetan–2–one at 168.1°C with solubility parameters of the solvents. (Rate constants from Ocampo, et al., 1997.)

as −6.7 cal/deg when the solvent was mesitylene and −10.8 cal/deg when the solvent was acetonitrile. This observation is consistent with there being more ordering or electrostriction in the polar solvent. A transition state that involves charge separation is consistent with this behavior.

Historically, solvent effects have been explained primarily in terms of the polarity or other characteristics of the solvent. While these cases illustrate the considerable role that the solubility parameter of the solvent has in influencing the rates of reactions, especially in organic chemistry, space does not permit a full consideration of the vast array of organic reaction types. Undoubtedly, reactions other than the substitution, esterification, and quaternization reactions described earlier are just as strongly influenced by the solvent. One of the best treatments of the broad area of solvent effects in organic chemistry is that given by Leffler and Grunwald (1989), which contains an enormous amount of information. However, that source, as well as most others, does not really do justice to the general application of solubility parameters to explaining rates of reactions. In fact, the solubility parameter is of tremendous importance in predicting solution properties and other facets of liquid state science (Hildebrand and Scott, 1962, 1949).

In this chapter, the basic principles of liquid state and solution behavior have been presented. These ideas form the basis for interpreting and understanding the role of the solvent in affecting the rates of chemical reactions from the standpoint of practical applications. Some additional approaches to describing solvent effects will be presented in Chapter 9.

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PROBLEMS

1. For the linkage isomerization reactions of

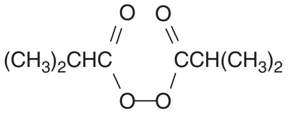
$$[M(NH_3)_5ONO]^{2+} \rightarrow [M(NH_3)_5NO_2]^{2+}$$

(where M = Co, Rh, or Ir) the activation parameters are as follows (Mares, M., Palmer, D. A., Kelm, H., *Inorg. Chim. Acta* 1978, *27*, 153).

	M = Co	M = Rh	M = Ir
$\Delta H^{\ddagger}$, kJ mol^{-1}	91.6 ± 0.8	80.2 ± 2.1	95.3 ± 1.3
$\Delta S^{\ddagger}$, J mol^{-1}K^{-1}	−17 ± 3	−33 ± 7	−11 ± 4

Test these data for an isokinetic relationship. Since the volumes of activation are -6.7 ± 0.4, -7.4 ± 0.4, and $-5.9 \pm 0.6\,\text{cm}^3\,\text{mol}^{-1}$, what mechanism is suggested for these isomerization reactons?

2. The decomposition of diisobutyrylperoxide,



produces C_3H_6,CO_2, and $(CH_3)_2COOH$. At 40°C, the following data were obtained (Walling, C., Waits, H. P., Milovanovic, J., Pappiaonnou, C. G., *J. Amer. Chem. Soc.* 1970, *92*, 4927).

Medium	10^5k, sec^{-1}
Gas	1
Cyclohexane	4.70
Nujol	4.63
Benzene	23.8
Acetonitrile	68.1

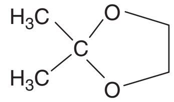
(a) In light of these data, speculate on the nature of the transition state for this reaction. From this general knowledge of the transition state, propose a mechanism for the reaction. (b) While the solvent effects were originally explained partially in terms of solvent polarity, determine the relationship between the solubility parameter of the solvent and k.

3. The viscosity of water and hexane vary with temperature as follows:

	t, °C	20	25	40	50
C_6H_{14}	η, cp	0.326	0.294	0.271	0.248
H_2O	η, cp	1.002	0.911	0.653	0.547

Determine the activation energy for viscous flow for these liquids. Explain why they are different.

4. The hydrolysis of 2, 2-dimethyl-1, 3-dioxolane,



has been studied in mixtures of water and glycerol as the solvent (Schaleger, L. L., Richards, C. N., *J. Amer. Chem. Soc.* 1970, *92*, 5565). Activation parameters are as follows.

% Glycerol	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
0	20.7	7.1
10	19.5	3.5
20	19.7	4.3
30	17.9	−1.6
40	17.6	−2.4

Analyze these data to determine whether a compensation effect is operative. If it is, determine the isokinetic temperature.

5. How should the following reactions depend on the ionic strength of the reaction medium?

(a) $[Pt(NH_3)_3Br]^+ + CN^- \rightarrow$
(b) $[PtCl_4]^{2-} + CN^- \rightarrow$
(c) $[Pt(NH_3)_2Cl_2] + Cl^- \rightarrow$

6. The solubility parameter for mixed solvents can be calculated using the equation

$$\delta_M = \sum_{i=1}^{n} X_i \delta_i$$

where X_i and δ_i are the mole fraction and solubility parameter for component i. The reaction

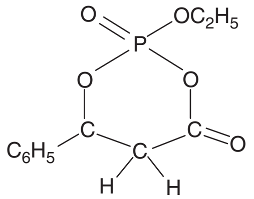
$$C_6H_5CH_2Cl + CN^- \rightarrow C_6H_5CH_2CN + Cl^-$$

has been studied in mixtures of H_2O and dimethylformamide, DMF. Results obtained were as follows (Jobe, K. I., Westway, K. C., *Can. J. Chem.* 1993, *71*, 1353).

Mole % DMF	$10^3 \times k$, $\mathbf{M}^{-1}s^{-1}$
2.5	4.40
5.0	3.20
15.0	0.52
20.0	0.57

(a) Use the data shown in Table 5.2 to determine the solubility parameters of the mixed solvents. (b) Test the relationship between ln k and δ for the solvents. (c) Discuss the probable mechanism of the reaction in light of the effect of δ on the rate.

7. The hydrolysis of



takes place in solution. The rate varies with pH as follows (Marecek, J. F., Griffith, D. L., *J. Am. Chem. Soc.* 1970, *92*, 917):

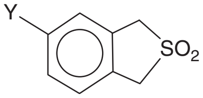
pH	0.5*	1.48	2.01	2.97	4.32	6.03	9.59	10.0	10.8
$10^3 x k_{obs}$	13*	6.64	5.90	5.83	5.04	5.05	8.31	11.3	23

*Estimated

Discuss what k_{obs} means in this case and describe a possible mechanism for the hydrolysis.

8. The decomposition of 2, 2-azoisobutane occurs in a 90:10 diphenylether:isoquinoline mixture with $\Delta H^{\ddagger} = 42.2$ kcal/mol and $\Delta S^{\ddagger} = 16.2$ cal/mol deg. In the gas phase, the values are 42.3 kcal/mol mol and 17.5 cal/mol deg, respectively. Explain what this signifies in terms of the transition state for the reaction. Speculate how the use of other solvents would likely affect the rate of the equation.

9. The hydrolysis of



has been studied where Y can be one of several different substituents (Zaborsky, O. R., Kaiser, E. T., *J. Am. Chem. Soc.* 1970, *92*, 860). The results obtained and the values of the para σ substituent constants (σ_p) are as follows.

Y	k, $\mathbf{M}^{-1}$ sec^{-1}	σ_p
H	37.4	0.00
NH_2	13.6	−0.66
OCH_3	21.3	−0.27
CH_3	24.0	−0.17
Br	95.1	0.23
NO_2	1430	1.24

Compare the rate constants for the groups to that for hydrogen and test the relationship between $\log(k_H/k_Y)$ and σ_p to determine if a linear free energy relationship exists. Provide an explanation for your results.

10. In most polar solvents such as dimethylformamide, the order of reactivity of halide ions in nucleophilic substitution is $Cl^- > Br^- > I^-$. However, in methanol the order of reactivity is reversed. Explain these observations in terms of the properties of the solvents and the nature of the transition state in each case.

CHAPTER 6

Enzyme Catalysis

Since the early study by Berzelius in 1835 to the preparation of the first crystalline enzyme in 1926 by Sumner and on to the present time, our knowledge of enzymes has grown at an increasing rate. Enzymes catalyze many important reactions that occur throughout the areas of biochemistry and physiology. These protein materials enable many such reactions to take place at low temperature under mild conditions, such as in living organisms. Some of the processes catalyzed by enzymes are also of commercial importance. For example, β-amylase is used to cleave maltose (a disaccharide) units from starch in the preparation of corn syrup. In the paper industry, α-amylase is used to cleave starch molecules to reduce the viscosity of starch pastes. These pastes are sprayed onto paper fibers to fill pores and provide a smooth surface (known as *paper sizing*).

Enzymes are high molecular weight proteins that are built from peptide chains. In their catalytic behavior, they provide a lower energy pathway for a reaction to take place. It is generally accepted that this occurs by the binding of the enzyme to the reactant, which is called the *substrate*, to form an enzyme-substrate complex, which renders the substrate more reactive in some specific way (Figure 6.1). We will describe the behavior of enzymes in more detail in the next section and then turn our attention to treating the kinetics of enzyme catalyzed processes.

6.1 ENZYME ACTION

Enzymes frequently function as catalysts in very specific ways. In general, four types of behavior can be described.

1. *Absolute specificity*. In this type of behavior, the enzyme catalyses a single reaction.

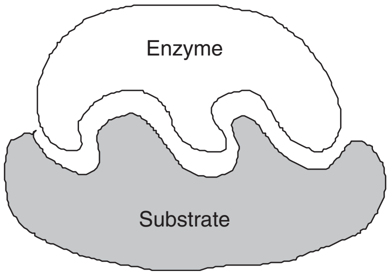


FIGURE 6.1 The "lock and key" model for the enzyme-substrate complex.

2. *Group specificity*. A reaction of only a single type of functional group is catalyzed by the enzyme.
3. *Linkage specificity*. In this case, the enzyme makes a specific type of bond labile.
4. *Stereochemical specificity*. Some enzymes catalyze reactions of only one stereoisomer of a compound.

In may cases, enzymes require the presence of another species before they are able to act as catalysts. Such additional species are called *cofactors*, and there are several types of cofactors known. The enzyme along with its cofactor is called the *holoenzyme*, while the protein portion alone is known as the *apoenzyme*.

Of the types of cofactors known, the most common are *coenzymes*, *prosthetic groups*, and *metal ions*. A coenzyme is some other organic material that is loosely attached to the protein enzyme (apoenzyme). If the organic compound is strongly attached to the apoenzyme, it called a *prosthetic group*.

Metal ions (e.g., Fe^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, Cu^{2+}, etc.) may enhance enzyme activity by binding to the enzyme (forming a complex). On the other hand, some materials known as *inhibitors* reduce the activity of enzymes. Such cases may result from competitive inhibition in which some material can bind to the enzyme preventing its attachment to the substrate (see Sec. 6.3.1). In another mode of enzyme inhibition, known as *noncompetitive inhibition* (discussed in Sec. 6.3.2), some material is present that binds to the enzyme, changing its configuration so that it can no longer bind to the substrate effectively. Substrate inhibition may occur when a large excess of substrate is present, which causes the equilibrium represented as

$$E + S \rightleftharpoons ES \tag{6.1}$$

(where E is the enzyme, S is the substrate, and ES is the enzyme-substrate complex) to lie far to the right so that most of the enzyme is effectively complexed.

Enzymes are protein materials and are, therefore, temperature sensitive. The thermal stress caused by temperatures as low as 40°C may be sufficient to cause denaturation of the protein, causing a loss of catalytic activity. These changes may be due to slight changes in configuration that can require only small energy changes. In a different configuration, the formation of the enzyme-substrate complex may be hindered, resulting in a decrease in the rate of the reaction. The typical variation in rate of an enzyme catalyzed reaction with temperature is shown in Figure 6.2. In general, the rate increases up to a certain temperature, and then decreases at higher temperature as denaturation of the enzyme takes place. Accordingly, as shown in Figure 6.2, enzymes usually have optimum effectiveness in a rather narrow range of temperature.

Since enzymes are proteins, they contain acidic and/or basic sites. Basic sites may become protonated at higher $[H^+]$ (low pH),

$$E + H^+ \rightleftharpoons H^+E \tag{6.2}$$

Acidic protons on the enzyme may be removed at high $[OH^-]$ (high pH),

$$E + OH^- \rightleftharpoons E^- + H_2O \tag{6.3}$$

Either of these conditions can alter the effectiveness of an enzyme to catalyze a reaction by changing the concentration of "free" enzyme. Therefore, a general relationship between enzyme activity and pH is shown in Figure 6.3. Most enzymes function effectively over a pH range of about 1.0 unit. In Section 6.4 the effect of pH on the rate of enzyme catalyzed reactions will be examined in greater detail.

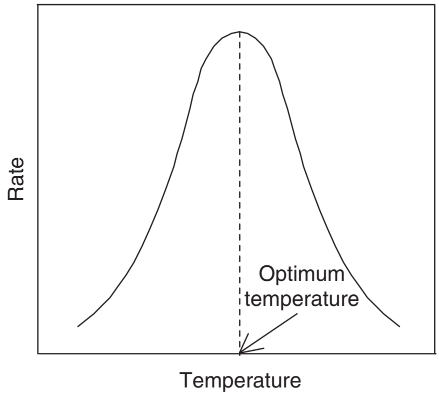


FIGURE 6.2 Dependence of most enzyme-catalyzed reactions on temperature.

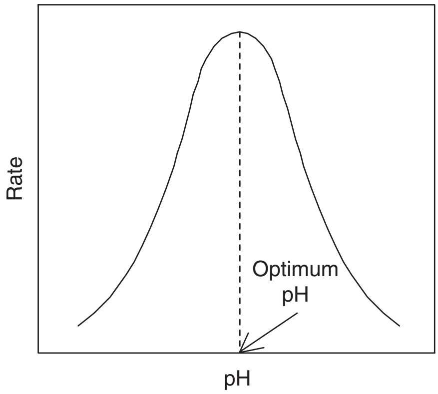


FIGURE 6.3 Dependence of most enzyme-catalyzed reactions on pH.

Enzymes are believed to function by complexing to the substrate by what is sometimes called the "lock and key" fashion that is represented in Figure 6.1. The sites where the configuration of the enzyme and substrate match are called *active sites*. This type of interaction makes it easy to see why the action of enzymes is highly specific in many cases.

6.2 KINETICS OF REACTIONS CATALYZED BY ENZYMES

Kinetic analysis of reactions catalyzed by enzymes is a difficult subject. However, many systems can be represented by rather simple kinetic models that have been successfully applied by many workers. While we will not treat some of the more esoteric and advanced topics associated with enzyme kinetics, a knowledge of the basic concepts is necessary for students in chemical kinetics and biochemistry. We will now describe these concepts in sufficient detail to provide a basis for further study of this important field.

6.2.1 Michaelis–Menten Analysis

When the concentration of substrate is varied over wide limits while the concentration of the enzyme is held constant, the reaction rate increases until a certain concentration of substrate is reached. This large concentration of substrate is sufficient to complex with all of the enzyme so any further increase in concentration of the substrate does not lead to the

formation of more enzyme-substrate complex and there is no further effect on the rate. This situation is similar to the decomposition of OCl^- described in Section 1.2.3 (a pseudo zero-order reaction).

We can show the equilibrium in this case as

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P + E \tag{6.4}$$

where P represents the product, k_1 and k_2 are rate constants for the forward reactions, and k_{-1} and k_{-2} are rate constants for the reverse reactions. In most cases, at least in the early stages, the concentration of the product is low so that the rate of the reverse reaction characterized by the rate constant k_{-2} can be neglected. Eventually, the rate of the reaction that leads to product formation (characterized by k_2[ES]) and that for decomposition of enzyme-substrate complex characterized by k_{-1}[ES] equals the rate of the formation of the enzyme-substrate complex, which is expressed as k_1[E][S]. Therefore, we can write

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \tag{6.5}$$

The total enzyme concentration, $[E]_t$, is equal to the sum of the concentration of free enzyme, [E], and that which is bound in the enzyme-substrate complex, [ES],

$$[E]_t = [E] + [ES] \tag{6.6}$$

Therefore,

$$[E] = [E]_t - [ES] \tag{6.7}$$

By substituting this value for [E] in Eq. (6.5) we obtain

$$k_1([E]_t - [ES])[S] = k_{-1}[ES] + k_2[ES] \tag{6.8}$$

Performing the multiplication of the left-hand side of this equation gives

$$k_1[E]_t[S] - k_1[ES][S] = k_{-1}[ES] + k_2[ES] \tag{6.9}$$

which can be rearranged to give

$$k_1[E]_t[S] = k_{-1}[ES] + k_2[ES] + k_1[ES][S] \tag{6.10}$$

Solving this equation for [ES] yields

$$[ES] = \frac{k_1[E]_t[S]}{k_{-1} + k_2 + k_1[S]} \tag{6.11}$$

Since the rate of product formation, which can be represented as R, is k_2[ES], after multiplying both sides by k_2, we can write

$$R = k_2[\mathrm{ES}] = \frac{k_1 k_2 [\mathrm{E}]_\mathrm{t}[\mathrm{S}]}{k_{-1} + k_2 + k_1[\mathrm{S}]} \tag{6.12}$$

Dividing both numerator and denominator by k_1 gives

$$R = \frac{k_2[\mathrm{E}]_\mathrm{t}[\mathrm{S}]}{\dfrac{k_{-1} + k_2}{k_1} + [\mathrm{S}]} \tag{6.13}$$

which can be simplified to obtain

$$R = \frac{k_2[\mathrm{E}]_\mathrm{t}[\mathrm{S}]}{\mathrm{K_m} + [\mathrm{S}]} \tag{6.14}$$

This equation is known as the Michaelis–Menten equation, and the constant $(k_{-1} + k_2)/k_1$ is called the Michaelis constant, $\mathrm{K_m}$.

When [S] is large compared to $\mathrm{K_m}$, the denominator of Eq. (6.14) is approximately [S] so that

$$R \approx \frac{k_2[\mathrm{E}]_\mathrm{t}[\mathrm{S}]}{[\mathrm{S}]} \approx k_2[\mathrm{E}]_\mathrm{t} \tag{6.15}$$

and the rate of the reaction under these conditions is the maximum rate, R_{max},

$$R_{\mathrm{max}} = k_2[\mathrm{E}]_\mathrm{t} \tag{6.16}$$

This situation is equivalent to saying that all of the enzyme is bound to the substrate in the enzyme-substrate complex. Therefore, from Eq. (6.14) we obtain

$$R = \frac{R_{\mathrm{max}}[\mathrm{S}]}{\mathrm{K_m} + [\mathrm{S}]} \tag{6.17}$$

In a situation where the substrate concentration is equal to $\mathrm{K_m}$,

$$R = \frac{R_{\mathrm{max}}[\mathrm{S}]}{[\mathrm{S}] + [\mathrm{S}]} = \frac{R_{\mathrm{max}}}{2} \tag{6.18}$$

Therefore, because $\mathrm{K_m} = (k_{-1} + k_2)/k_1$,$\mathrm{K_m}$ is also equal to the concentration of substrate when the reaction rate is half its maximum value. This is shown graphically in Figure 6.4.

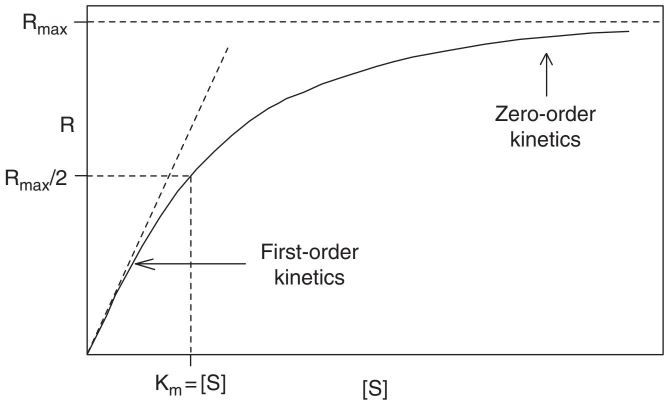


FIGURE 6.4 Reaction rate versus substrate concentration for a reaction following Michaelis–Menten kinetics.

When the substrate concentration is much larger than the value of K_m, $[S] >> K_m$,

$$R = \frac{k_2[E]_t[S]}{K_m + [S]} \approx \frac{k_2[E]_t[S]}{[S]} = k_2[E]_t \tag{6.19}$$

and the rate of the reaction is independent of the concentration of the substrate; the reaction follows a zero-order rate law with respect to substrate concentration. On the other hand, when $K_m >> [S]$, we can write

$$R = \frac{R_{max}[S]}{K_m + [S]} \approx \frac{k_2[E]_t[S]}{K_m} \tag{6.20}$$

which shows that the reaction is first-order with respect to substrate concentration. The two regions where the reaction is first-order and zero-order with respect to substrate are also shown in Figure 6.4.

The Michaelis constant is a fundamental characteristic of an enzyme that incorporates important information about the enzyme. First, it gives the concentration of substrate necessary to bind to half of the available sites on the enzyme. Second, it gives an index of the relative binding affinity of the substrate to the active sites on the enzyme. Michaelis constants have been determined and tabulated for a large number of enzymes. Since K_m is actually a concentration, the values are usually expressed in m**M** units.

The Michaelis–Menten treatment of enzyme catalyzed reactions bears a striking resemblance to the treatment of heterogeneous catalysis described in Chapter 4. Both treatments deal with the attachment of the reactant at

active sites, one on an enzyme and the other on the surface of a solid. Both cases also apply the steady state approximation to the formation of "activated" reactant. Compare Figures 4.8 and 6.4 to see this similarity graphically and compare the forms of Eqs. (4.169) and (6.14) to see the similarity in the forms of the mathematical rate laws.

While the limiting cases of the Michaelis–Menten approach have been illustrated by the earlier and later portions of the plot shown in Figure 6.4, it is also possible to deal with Eq. (6.14) by direct integration. With the equation written in differential form, we have

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_2[\mathrm{E}]_\mathrm{t}[\mathrm{S}]}{\mathrm{K_m} + [\mathrm{S}]} \tag{6.21}$$

Dividing both sides of this equation by $[\mathrm{S}]/(\mathrm{K_m} + [\mathrm{S}])$ gives

$$\frac{-\dfrac{d[\mathrm{S}]}{dt}}{\dfrac{[\mathrm{S}]}{\mathrm{K_m} + [\mathrm{S}]}} = k_2[\mathrm{E}]_\mathrm{t} \tag{6.22}$$

which can also be written as

$$-\frac{d[\mathrm{S}]}{dt} \cdot \frac{\mathrm{K_m} + [\mathrm{S}]}{[\mathrm{S}]} = k_2[\mathrm{E}]_\mathrm{t} \tag{6.23}$$

We can now rearrange this equation to obtain

$$-d[\mathrm{S}]\left(\frac{\mathrm{K_m}}{[\mathrm{S}]} + 1\right) = k_2[\mathrm{E}]_\mathrm{t}dt \tag{6.24}$$

which can also be written in the form

$$-\mathrm{K_m} \cdot \frac{d[\mathrm{S}]}{[\mathrm{S}]} - d[\mathrm{S}] = k_2[\mathrm{E}]_\mathrm{t}dt \tag{6.25}$$

Integrating this equation between limits $[\mathrm{S}]_\mathrm{o}$ at $t = 0$ and [S] at time t, we obtain

$$\mathrm{K_m} \ln\frac{[\mathrm{S}]_\mathrm{o}}{[\mathrm{S}]} + ([\mathrm{S}]_\mathrm{o} - [\mathrm{S}]) = k_2[\mathrm{E}]_\mathrm{t}t \tag{6.26}$$

The first term on the left-hand side of this equation shows the first-order dependence of the rate, while the second term $([\mathrm{S}]_\mathrm{o} - [\mathrm{S}])$, shows the zero-order dependence. Figure 6.4 illustrates that the reaction begins as a process that is first-order in substrate and then shifts to a zero-order dependence.

The parallel between surface-catalyzed reactions described in Chapter 4 and enzyme-catalyzed processes has already been mentioned. However a comparison of Eq. (6.26) with Eq. (4.182), which is written as

$$\frac{1}{K}\ln\frac{P_{A,o}}{P_A}+(P_{A,o}-P_A)=kt \tag{6.27}$$

shows this similarity clearly. The surface-catalyzed reaction also shows the transition from first-order to zero-order kinetics as the reaction proceeds. It should be pointed out that sometimes assuming similar mechanistic features can result in equivalent mathematical models in widely differing branches of chemical kinetics. This is an intriguing feature of kinetic studies. For example, an equation found to be applicable to describing one type of solid state reaction is also applicable to describing some types of fluorescence.

6.2.2 Lineweaver–Burk and Eadie Analyses

Several methods have been developed for analyzing rate data for enzyme-catalyzed reactions. One of the most commonly used methods is based on writing Eq. (6.14) in the reciprocal form

$$\frac{1}{R}=\frac{K_m+[S]}{k_2[E]_t[S]}=\frac{K_m}{k_2[E]_t[S]}+\frac{[S]}{k_2[E]_t[S]} \tag{6.28}$$

As a result, the working equation is written in the form

$$\frac{1}{R}=\frac{K_m}{k_2[E]_t[S]}+\frac{1}{k_2[E]_t} \tag{6.29}$$

which shows that when $1/R$ is plotted versus the reciprocal of the substrate concentration, a straight line results, the slope of which is $K_m/k_2[E]_t$ and the intercept is $1/k_2[E]_t$. Such a plot, known as a Lineweaver–Burk or double reciprocal plot, is shown in Figure 6.5. A major disadvantage of this procedure is that most of the data are obtained at relatively high substrate concentrations so that the extrapolation of the line to low values of [S] may be somewhat inaccurate.

If Eq. (6.29) is multiplied by [S], one obtains

$$\frac{[S]}{R}=\frac{[S]}{k_2[E]_t}+\frac{K_m}{k_2[E]_t} \tag{6.30}$$

Therefore, a plot of $[S]/R$ versus [S] will be linear with a slope of $1/k_2[E]_t$, which is equal to $1/R_{max}$ and an intercept of $K_m/k_2[E]_t$, which is K_m/R_{max}.

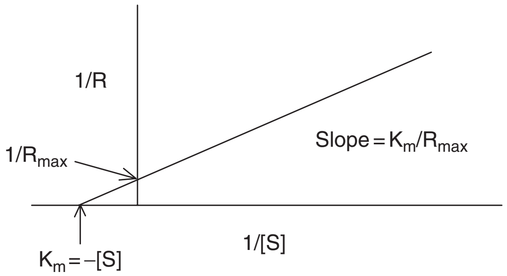


FIGURE 6.5 A Lineweaver–Burk plot for an enzyme-catalyzed reaction.

This type of plot is known as a Hanes–Wolf plot, and it is illustrated in Figure 6.6.

Another method of analyzing data for enzyme-catalyzed reactions utilizes Eq. (6.14) written in the form

$$R(\mathrm{K_m} + [\mathrm{S}]) = k_2[\mathrm{E}]_t[\mathrm{S}] \tag{6.31}$$

Performing the multiplication on the left-hand side of this equation gives

$$R\mathrm{K_m} + R[\mathrm{S}] = k_2[\mathrm{E}]_t[\mathrm{S}] \tag{6.32}$$

Dividing both sides of this equation by [S] gives

$$\frac{R\mathrm{K_m}}{[\mathrm{S}]} + R = k_2[\mathrm{E}]_t \tag{6.33}$$

This equation shows that a plot of R versus $R/[\mathrm{S}]$ should result in a line that has a slope of $-\mathrm{K_m}$ and an intercept of $k_2[\mathrm{E}]_t$. A plot of this type is known as an Eadie–Hofstee plot, and it is illustrated graphically in Figure 6.7. The methods of data analysis that are based on Eqs. (6.29) and (6.33) are called *single reciprocal methods*.

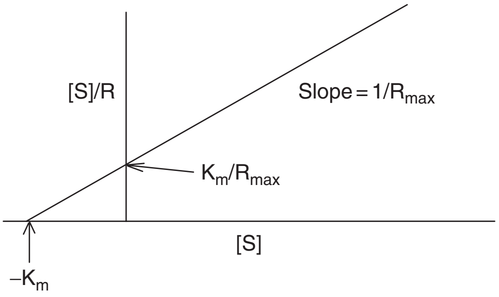


FIGURE 6.6 A Hanes–Wolff (single reciprocal) plot.

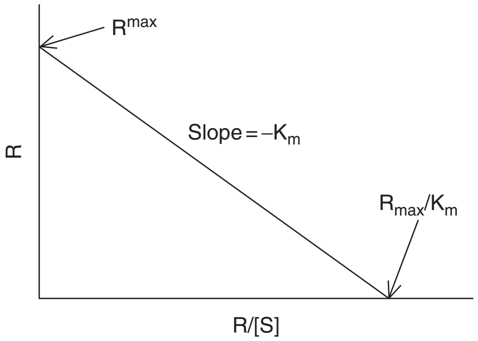


FIGURE 6.7 An Eadie–Hofstee (single reciprocal) plot.

In the previous sections, we described some of the ways in which analyses of data from kinetic studies on enzyme-catalyzed reactions are carried out. This is an active and important area of research, and many interesting and unusual aspects of reactions of this type are still being developed. Because of space constraints, it is not possible to describe the enormous number of systems that have been studied.

6.3 INHIBITION OF ENZYME ACTION

Although enzymes are protein materials having high molecular weights, some substrates are small molecules. For example, the decomposition of hydrogen peroxide (molecular weight 34) is catalyzed by the enzyme *catalyase*, which has a molecular weight of about 250,000. The enzyme lowers the activation energy for decomposition of H_2O_2 from 75 kJ/mol to about 8 kJ/mol. For many enzymes, the active site is localized to a small region of the much larger molecule. If some substance becomes bound to the active site of the enzyme, part or all of the ability of the enzyme to function as a catalyst is lost. The enzyme *urease* catalyzes the conversion of urea to NH_3 and CO_2. However, *urease* is strongly affected by metal ions such as Ag^+, Pt^{2+}, Hg^{2+}, and Pt^{2+}, which decrease the activity of the enzyme. Such substances that function in this way are called *inhibitors*. It is the inhibition of the enzyme activity of *peroxidase*, *catalase*, and *cytochrome oxidase* that causes HCN, H_2S, and azides to be extremely toxic. Certain drugs act as inhibitors for the action of some enzymes. Consequently, it is essential that some discussion of the action of inhibitors be presented on this

important aspect of enzyme action. The three simplest kinetic models for enzyme inhibition are competitive inhibition, noncompetitive inhibition, and uncompetitive inhibition, and these will be discussed by showing the mathematical treatment of enzyme kinetics.

6.3.1 Competitive Inhibition

We earlier described enzyme action in terms of the active site hypothesis. If an inhibiting substance can bind at the enzyme active site, there will be competition between the substrate, S, and the inhibitor, I, for the enzyme. The enzyme that is bound in a complex with the inhibitor, EI, is not available for binding with the substrate, so the effectiveness of the enzyme will be diminished. The chemical process for the formation of the product can be represented as

$$\mathrm{E + S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{P + E} \tag{6.34}$$

The concentration of the enzyme-inhibitor complex, EI, is determined by the equilibrium

$$\mathrm{E + I} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{EI} \tag{6.35}$$

In this system, the concentration of "free" enzyme, [E], is the total concentration, $[\mathrm{E}]_\mathrm{t}$, minus the amount bound in the ES and EI complexes. Writing the expression for the equilibrium constant and substituting for [E] gives

$$\mathrm{K} = \frac{[\mathrm{EI}]}{[\mathrm{E}][\mathrm{I}]} = \frac{k_3}{k_{-3}} = \frac{[\mathrm{EI}]}{([\mathrm{E}]_t - [\mathrm{ES}] - [\mathrm{EI}])[\mathrm{I}]} \tag{6.36}$$

If we let $\mathrm{K_i}$ represent the equilibrium constant for *dissociation* of the EI complex, then $\mathrm{K_i} = 1/\mathrm{K}$, and solving the resulting expression for [EI] gives

$$[\mathrm{EI}] = \frac{[\mathrm{I}]([\mathrm{E}]_\mathrm{t} - [\mathrm{ES}])}{\mathrm{K_i} + [\mathrm{I}]} \tag{6.37}$$

For the complex ES, the change in concentration with time is the difference between the rate at which ES is formed and the rate at which it dissociates. Therefore, after a steady state is reached,

$$\frac{d[\mathrm{ES}]}{dt} = k_1([\mathrm{E}]_\mathrm{t} - [\mathrm{ES}] - [\mathrm{EI}])[\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}] = 0 \qquad (6.38)$$

where $[\mathrm{E}]_\mathrm{t}$ is the total concentration of the enzyme. Substituting for [EI] the result from Eq. (6.37) yields upon rearranging and substituting for $\mathrm{K_m} = (k_{-1} + k_2)/k_1$,

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_\mathrm{t}[\mathrm{S}]\mathrm{K_i}}{[\mathrm{S}]\mathrm{K_i} + \mathrm{K_m}\mathrm{K_i} + \mathrm{K_m}[\mathrm{I}]} \qquad (6.39)$$

Because the rate of formation of product is given by

$$R = k_2[\mathrm{ES}] \qquad (6.40)$$

the rate can now be expressed as

$$R = \frac{k_2[\mathrm{E}]_\mathrm{t}[\mathrm{S}]\mathrm{K_i}}{[\mathrm{S}]\mathrm{K_i} + \mathrm{K_m}\mathrm{K_i} + \mathrm{K_m}[\mathrm{I}]} \qquad (6.41)$$

The rate has a maximum (R_{max}) when [S] is large, so under these conditions the rate can be expressed as $k_2[\mathrm{E}]_\mathrm{t}$. Therefore, substituting for $k_2[\mathrm{E}]_\mathrm{t}$ in Eq. (6.41) yields

$$R = \frac{R_{\mathrm{max}}[\mathrm{S}]\mathrm{K_i}}{[\mathrm{S}]\mathrm{K_i} + \mathrm{K_m}\mathrm{K_i} + \mathrm{K_m}[\mathrm{I}]} \qquad (6.42)$$

Writing this equation in terms of $1/R$ and rearranging gives

$$\frac{1}{R} = \frac{1}{R_{\mathrm{max}}}\left(\mathrm{K_m} + \frac{\mathrm{K_m}[\mathrm{I}]}{\mathrm{K_i}}\right)\frac{1}{[\mathrm{S}]} + \frac{1}{R_{\mathrm{max}}} \qquad (6.43)$$

which is usually written in the form

$$\frac{1}{R} = \frac{\mathrm{K_m}}{R_{\mathrm{max}}}\left(1 + \frac{[\mathrm{I}]}{\mathrm{K_i}}\right)\frac{1}{[\mathrm{S}]} + \frac{1}{R_{\mathrm{max}}} \qquad (6.44)$$

This equation indicates that a graph of $1/R$ versus $1/[\mathrm{S}]$ should be linear with a slope of $(\mathrm{K_m}/R_{\mathrm{max}})(1 + [\mathrm{I}]/\mathrm{K_i})$ and an intercept on the y-axis of $1/R_{\mathrm{max}}$. For different concentrations of inhibitor, a family of lines will be obtained that are characteristic of different [I] values. The graphical application of this analysis is shown in Figure 6.8.

When the concentration of inhibitor is varied and a family of lines having a common intercept as shown in Figure 6.8 is obtained, it is usually considered as a diagnostic test for a case of competitive inhibition and that the inhibitor is functioning in that manner.

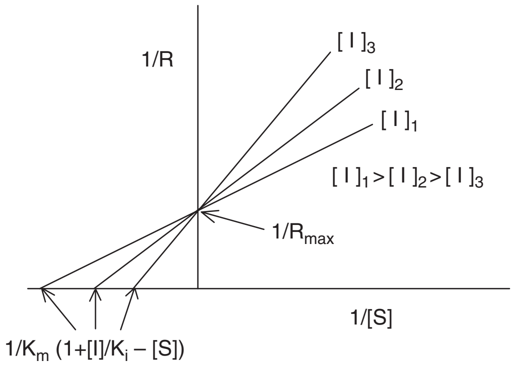


FIGURE 6.8 A Lineweaver–Burk plot for the case of competitive enzyme inhibition at three concentrations of inhibitor.

6.3.2 Noncompetitive Inhibition

In noncompetitive inhibition, the inhibitor is presumed not to bind to an active site on the enzyme, but rather to bind at some other site. This complex formation may involve some change in the conformation of the enzyme, which makes it impossible for the substrate to bind at the active site. The inhibition of *urease* by Ag^+, Pb^{2+}, or Hg^{2+} is believed to be the result of these metal ions binding to the sulfhydryl (–SH) groups on the enzyme. For this type of action, we can write the equilibria

$$E + I \rightleftharpoons EI \tag{6.45}$$

$$ES + I \rightleftharpoons ESI \tag{6.46}$$

where both EI and ESI are complexes of the enzyme that are inactive with respect to the formation of product. In this case, the equilibrium constants K_i^{EI} and K_i^{ESI} are the equilibrium constants for the dissociation of the complexes EI and ESI, respectively. Following a procedure similar to that illustrated in the last section, it is possible to derive the equation

$$\frac{1}{R} = \frac{K_m}{R_{max}}\left(1 + \frac{[I]}{K_i}\right)\frac{1}{[S]} + \frac{1}{R_{max}}\left(1 + \frac{[I]}{K_i}\right) \tag{6.47}$$

In this equation, K_i represents the combined effects of both K_i^{EI} and K_i^{ESI}. This equation indicates that a plot of $1/R$ versus $1/[S]$ should be linear with a slope that represents $(K_m/R_{max})(1 + [I]/K_i)$ and an intercept of $(1/R_{max})(1 + [I]/K_i)$. A different line will be obtained for each initial

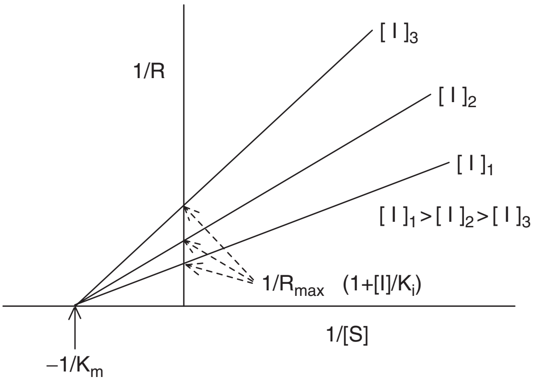


FIGURE 6.9 A Lineweaver–Burk plot for the case of noncompetitive enzyme inhibition at three concentrations of the inhibitor.

value of [I] used, but the lines have a common intercept of $1/K_m$ on the *x*-axis. This situation is illustrated graphically in Figure 6.9, and when this behavior is observed, it is usually taken as a diagnostic test indicating noncompetitive inhibition.

6.3.3 Uncompetitive Inhibition

The model of uncompetitive inhibition describes a case in which the inhibitor combines reversibly with the enzyme-substrate complex after it forms. Further, it is assumed that this complex is so stable that it does not lead to formation of the expected product. If this were not so, this case would reduce to a special case of noncompetitive inhibition. The formation of the inactive complex, ESI, is written as

$$ES + I \rightleftharpoons ESI \tag{6.48}$$

The equilibrium constant for this reaction can be written as

$$K = \frac{[ESI]}{[ES][I]} \tag{6.49}$$

Following the procedures analogous to those used in describing the other types of inhibition, we can derive the equation

$$\frac{1}{R} = \frac{K_m}{R_{max}} \frac{1}{[S]} + \frac{1}{R_{max}} \left(1 + \frac{[I]}{K_i}\right) \tag{6.50}$$

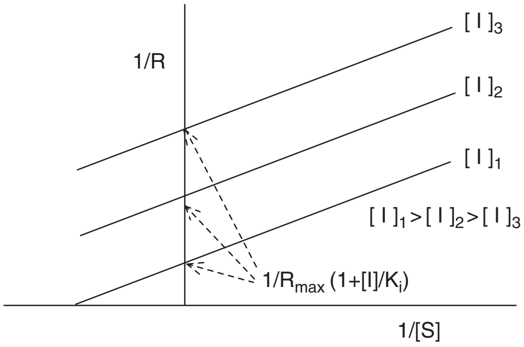


FIGURE 6.10 A Lineweaver–Burk plot for the case of uncompetitive inhibition at three concentrations of inhibitor.

Equation (6.50) shows that a plot of $1/R$ versus $1/[S]$ will be linear with a slope of K_m/R_{max} and an intercept of $1/R_{max}(1 + [I]/K_i)$. In fact, for a series of concentrations of the inhibitor, a series of lines of identical slope (K_m/R_{max}) will be obtained. The intercepts will be related to [I] because the intercept is given by $1/R_{max}(1 + [I]/K_i)$. This situation is shown graphically in Figure 6.10.

From the discussion presented, it should be apparent that enzyme inhibition is an important but complicating aspect of the study of the kinetics of enzyme-catalyzed reactions. Although it will not be discussed in detail, another type of inhibition occurs when a product forms a stable complex with the enzyme. This leads to a decrease in the rate of the reaction not only because some substrate is consumed, but also because of the decrease in the effective concentration of the enzyme. For additional details on enzyme inhibition, consult the references listed at the end of this chapter.

6.4 THE EFFECT OF pH

Earlier in this chapter, it was mentioned that many enzymes show greatest activity over a rather narrow range of pH. The principles described in previous sections provide the basis for a more detailed explanation of the effect of pH by making use of the Michaleis–Menten procedure. In general, an enzyme has one or more sites where H^+ can be removed or H^+ can be added depending on the acidity of the solution. Therefore, we will represent the enzyme concentration as EH, the deprotonated enzyme as E^-, and

the protonated enzyme as EH_2^+. The equilibria involved can be shown as follows.

$$\begin{array}{l} E^- + H^+ \\ K_2 \uparrow\downarrow \\ EH + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EHS \xrightarrow{k_2} EH + P \\ K_1 \downarrow\uparrow \\ EH_2^+ \end{array} \tag{6.51}$$

For this system, the total enzyme concentration is

$$E_t = EH + E^- + EH_2^+ + EHS \tag{6.52}$$

There are three equilibrium constants to be considered, those for proton removal and addition (K_2 and K_1, respectively, for *dissociation* of the protonated species) and that for the *dissociation* of the EHS complex (K_s). These can be written as

$$K_1 = \frac{[EH][H^+]}{[EH_2^+]} \qquad K_2 = \frac{[E^-][H^+]}{[EH]} \qquad K_s = \frac{[EH][S]}{[EHS]} \tag{6.53}$$

From Eq. (6.52), substitution for the concentrations of species obtained from the expressions for the equilibrium constants gives

$$[E]_t = \frac{[E^-][H^+]}{K_2} + \frac{K_2[EH]}{[H^+]} + \frac{[EH][H^+]}{K_1} + [EHS] \tag{6.54}$$

Dividing each side of this equation by [EHS] gives

$$\frac{[E]_t}{[EHS]} = \frac{[E^-][H^+]}{K_2[EHS]} + \frac{K_2[EH]}{[H^+][EHS]} + \frac{[EH][H^+]}{K_1[EHS]} + 1 \tag{6.55}$$

Substituting $[EH][S]/K_s$ for [EHS] on the right-hand side of this equation yields

$$\frac{[E]_t}{[EHS]} = \frac{[E^-][H^+]K_s}{K_2[EH][S]} + \frac{K_2[EH]K_s}{[H^+][EH][S]} + \frac{[EH][H^+]K_s}{K_1[EH][S]} + 1 \tag{6.56}$$

Canceling [EH] in the second and third terms on the right-hand side and recognizing from the expression for K_2 that $[E^-][H^+]/K_2[H] = 1$, we obtain

$$\frac{[E]_t}{[EHS]} = \frac{K_s}{[S]} + \frac{K_2}{[H^+]} \times \frac{K_s}{[S]} + \frac{[H^+]}{K_1} \times \frac{K_s}{[S]} + 1 = 1 + \frac{K_s}{[S]}\left(1 + \frac{K_2}{[H^+]} + \frac{[H^+]}{K_1}\right) \tag{6.57}$$

Solving this equation for [EHS] gives

$$[\mathrm{EHS}] = \frac{[\mathrm{E}]_t}{1 + \dfrac{K_s}{[\mathrm{S}]}\left(1 + \dfrac{K_2}{[\mathrm{H}^+]} + \dfrac{[\mathrm{H}^+]}{K_1}\right)} \tag{6.58}$$

The rate of the formation of product is expressed as $R = k_2[\mathrm{EHS}]$ so

$$R = k_2[\mathrm{EHS}] = \frac{k_2[\mathrm{E}]_t}{1 + \dfrac{K_s}{[\mathrm{S}]}\left(1 + \dfrac{K_2}{[\mathrm{H}^+]} + \dfrac{[\mathrm{H}^+]}{K_1}\right)} \tag{6.59}$$

Writing $1 = [\mathrm{S}]/[\mathrm{S}]$ in the denominator, collecting terms, and simplifying gives

$$R = \frac{k_2[\mathrm{E}]_t[\mathrm{S}]}{[\mathrm{S}] + K_s\left(1 + \dfrac{K_2}{[\mathrm{H}^+]} + \dfrac{[\mathrm{H}^+]}{K_1}\right)} \tag{6.60}$$

This equation is of the same form as that of Michaelis–Menten shown in Eq. (6.14) with

$$K_m = K_s\left(1 + \frac{K_2}{[\mathrm{H}^+]} + \frac{[\mathrm{H}^+]}{K_1}\right) \tag{6.61}$$

None of the factors in numerator of the expression for R contain $[\mathrm{H}^+]$ so the *maximum* rate, R_{max}, does not depend on pH. At low pH where $[\mathrm{H}^+]$ is relatively high, the term $K_2/[\mathrm{H}^+]$ is small compared to $[\mathrm{H}^+]/K_1$ in the denominator of Eq. (6.60), so

$$R \approx \frac{R_{max}[\mathrm{S}]}{[\mathrm{S}] + K_s\left(1 + \dfrac{[\mathrm{H}^+]}{K_1}\right)} \tag{6.62}$$

By dividing the numerator and denominator on the right-hand side by K_1, Eq. (6.42) can be put into a form equivalent to Eq. (6.62). In other words, this situation is equivalent to competitive inhibition in which H^+ acts as the inhibitor.

Using Eq. (6.61), it is possible to construct a curve showing how the value of the Michaelis constant varies with pH. To do this, we need to assume values for K_s, K_1, and K_2, which will be taken as 5×10^{-4},10^{-5}, and 10^{-7}, respectively. By varying $[\mathrm{H}^+]$, values can be computed for K_m. To simplify the drawing, we will calculate the negative logarithm of K_m

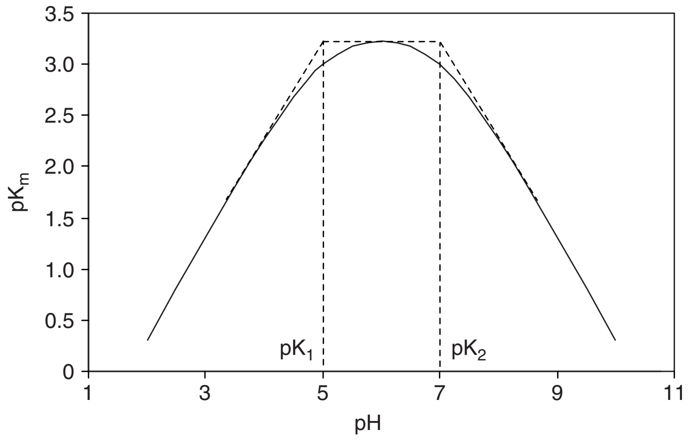


FIGURE 6.11 A plot of the logarithm of the apparent K_m versus pH for the enzyme-catalyzed process shown in Eq. (6.51). The dissociation constant for the EHS complex was taken as 5.0×10^{-4}, K_1 as 10^{-5} mol/l, and K_2 as 10^{-7}mol/l.

(which is pK_m) and plot that quantity versus pH. Values used for $[H^+]$ range from 10^{-2} to 10^{-10} (pH = 2 to pH = 10). The results of the calculations are shown in Figure 6.11.

As expected, the calculated values for K_m go through a maximum and decrease on either side. In this case, because of the way the values were chosen, the maximum rate occurs at a pH of 6. If a sufficient number of values for $[H^+]$ are utilized so that several data points are obtained, the lower extremities of the curve can be approximated as straight lines that intersect a horizontal line drawn tangent to the top of the curve. The values of the points on the pH axis can be shown to represent the values of pK_1 and pK_2. Although there are other possible scenarios for interpreting effects of pH on enzyme activity, the approach shown here leads to the conclusion that has been verified by many experimental systems. Enzymes usually function best over a rather narrow range of pH and there is some optimum pH for a particular enzyme.

6.5 ENZYME ACTIVATION BY METAL IONS

Earlier we mentioned the fact that certain enzymes exhibit enhanced activity in the presence of specific metal ions. For example, Mg^{2+} plays a

role in phosphorylation reactions of adenosine triphosphate (ATP). The process can be represented as

$$\begin{array}{c} \mathrm{O}\quad\ \ \mathrm{O}\quad\ \ \mathrm{O} \qquad\qquad\qquad\qquad\quad \mathrm{O}\quad\ \ \mathrm{O}\qquad\qquad\quad\ \ \mathrm{O} \\ |\qquad\ |\qquad\ | \qquad\qquad\qquad\qquad\quad |\qquad\ |\qquad\qquad\quad\ \ | \\ \mathrm{A-O-P-O-P-O-P-O^-} \xrightarrow[\mathrm{H_2O}]{\mathrm{Mg^{2+}}} \mathrm{A-O-P-O-P-O^-} + \mathrm{HO-P-O^-} \\ |\qquad\ |\qquad\ | \qquad\qquad\qquad\qquad\quad |\qquad\ |\qquad\qquad\quad\ \ | \\ \mathrm{O}\quad\ \ \mathrm{O}\quad\ \ \mathrm{O} \qquad\qquad\qquad\qquad\quad \mathrm{O}\quad\ \ \mathrm{O}\qquad\qquad\quad\ \ \mathrm{O} \end{array} \tag{6.63}$$

The product, $A{-}OP_2O_6^-$ is adenosine diphosphate, ADP. The transfer of a phosphate group is also assisted by a metal ion in the reaction between glucose and ATP.

$$\text{Glucose} + \text{ATP} + \text{Mg}^{2+} \rightarrow \text{Glucose-6-phosphate} + \text{ADP} + \text{Mg}^{2+} \tag{6.64}$$

A reaction scheme that illustrates the role of the metal ion in the enzyme activity can be shown by the following reactions, in which E represents the enzyme, S is the substrate, M is the metal ion, P is the product, and EM is the enzyme-metal complex. The rate constant for the formation of the enzyme-metal complex is k_m and that for its dissociation is k_{-m}.

$$\mathrm{E} + \mathrm{M} \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} \mathrm{EM} \tag{6.65}$$

$$\mathrm{EM} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{EMS} \xrightarrow{k_2} \mathrm{E} + \mathrm{P} + \mathrm{M} \tag{6.66}$$

It is possible to analyze this mechanism by means of the stationary state approximation to obtain

$$R = \frac{R_{max}[\mathrm{M}][\mathrm{S}]}{\mathrm{K_m} + \mathrm{K_m}[\mathrm{M}] + [\mathrm{S}][\mathrm{M}] + \mathrm{K_{EM}}} \tag{6.67}$$

where K_m is the apparent Michaelis constant and K_{EM} is the equilibrium constant for the first step, which is given by k_m/k_{-m}. Equation (6.67) shows that for a given concentration of substrate, the rate varies with metal ion concentration and approaches a maximum value of $R_{max}[S]$.

6.6 REGULATORY ENZYMES

Although the kinetic analysis of enzyme-catalyzed reactions has been illustrated by application of the Michaelis–Menten model, not all enzymes react in a way that follows this type of behavior. Enzymes that catalyze

reactions in such a way that the Michaelis–Menten kinetics is observed are called *nonregulatory enzymes*. *Regulatory* enzymes are those that are involved in a metabolic pathway, and they often give plots of rate versus [S] that are sigmoidal. In fact, this feature is frequently the distinguishing characteristic of regulatory enzymes. Because the kinetic behavior of regulatory enzymes does not follow the Michaelis–Menten model, the double reciprocal or Lineweaver–Burk plots will not be linear. Regulatory enzymes are sometimes compared by means of a parameter R_s, which is defined by the equation

$$R_s = \frac{\text{Substrate concentration at } 0.9\ R_{max}}{\text{Substrate concentration at } 0.1\ R_{max}} \tag{6.68}$$

For an enzyme that follows Michaelis–Menten kinetics, $R_s = 81$. For a regulatory enzyme that gives a sigmoidal rate plot, $R_s < 81$ if the enzyme is exhibiting *positive cooperativity*, a term that means that the substrate and enzyme bind in such a way that the rate increases to a *greater* extent with increasing [S] than the Michaelis–Menten model predicts. Cases with $R_s > 81$ indicate *negative cooperativity* so that the catalytic effect becomes *less* than that found in Michaelis–Menten kinetics. In these cases, kinetic analysis is usually carried out by means of the Hill equation,

$$\frac{R}{R_{max}} = \frac{[S]^n}{[S]^n + K'} \tag{6.69}$$

where K′ is called the *binding constant* and *n* is the number of occupied sites on the enzyme where the substrate can bind. After taking the reciprocal of both sides, this equation can be arranged to give

$$\frac{R_{max} - R}{R} = \frac{K'}{[S]^n} \tag{6.70}$$

which can also be written as

$$\frac{R}{R_{max} - R} = \frac{[S]^n}{K'} \tag{6.71}$$

Taking the logarithm of both sides of this equation gives

$$\log\frac{R}{R_{max} - R} = n\log[S] - \log K' \tag{6.72}$$

Therefore, a graph showing $\log(R/(R_{max} - R))$ versus log [S] should give a straight line having a slope of *n* and an intercept of $-\log K'$. Such a graph is

known as a Hill plot. The terms noncooperativity, negative cooperativity, and positive cooperativity are applied to cases where $n = 1$, $n < 1$, and $n > 1$, respectively. When the rate of the reaction is half of its maximum value, $R = R_{max}/2$. Substituting this value in Eq. (6.72) gives

$$\log \frac{R_{max}/2}{R_{max} - R_{max}/2} = \log 1 = 0 \tag{6.73}$$

Therefore,

$$n \log [S] = \log K' \tag{6.74}$$

so taking the antilogarithms of both sides gives

$$[S]^n = K' \tag{6.75}$$

or

$$[S] = \sqrt[n]{K'} \tag{6.76}$$

It should be pointed out that sigmoidal rate plots are sometimes observed for reactions of solids. One of the rate laws used to model such reactions is the Prout–Tompkins equation, the left-hand side of which contains the function $\ln(\alpha/(1 - \alpha))$ where α is the fraction of the sample reacted (see Section 7.4). The left-hand sides of Eqs. (6.72) and (7.68) have the same form, and both result in sigmoidal rate plots. These cases illustrate once again how greatly different types of chemical processes can give rise to similar rate expressions.

Although we have described a few of the types of inhibition of enzyme action, several other types are known, and they have been described mathematically. An introductory book such as this can provide only a survey of the vast field of enzyme kinetics so this important and rapidly growing branch of science cannot be treated fully here. The introduction provided should be sufficient for the nonspecialist in the field.

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PROBLEMS

1. For an enzyme catalyzed reaction, the following data were obtained.

[S], **M**	Rate, $\mathbf{M}^{-1}$ min^{-1}
0.005	0.0143
0.010	0.0208
0.025	0.0294
0.050	0.0345
0.075	0.0360

Using these data, determine the Michaelis constant for this enzyme system.

2. The reaction described in Question 1 was also carried out in the presence of an inhibitor, X, with the concentration of this inhibitor being 2.0×10^{-4} **M**. Under these conditions the rate varied with substrate concentration as follows.

[S], **M**	Rate, $\mathbf{M}^{-1}$sec^{-1}
0.005	0.0080
0.010	0.0133
0.025	0.0222
0.050	0.0286
0.075	0.0323

(a) Analyze these data to determine the type of inhibition that is caused by X. (b) Determine R_{max}.

3. The initial rate, V, of an enzyme catalyzed reaction varies with substrate concentration as follows:

[S], **M**	$10^6 \times$ Initial rate, $\mathbf{M}s^{-1}$
0.020	0.585
0.004	0.495
0.002	0.392
0.001	0.312
0.00066	0.250

Determine V_{max} and K_m for this reaction.

4. For an enzyme catalyzed reaction, the initial rate R_o was determined at each initial concentration of substrate $[S]_o$. The following data were obtained.

$[S]_o$, μ M/l	R_o, μ M/l
1	2.5
5	9.8
10	20.2
20	31.7
30	41.2
50	50.2
100	60.1
500	74.3

(a) Use these data to determine K_m and R_{max} by means of a Lineweaver–Burke–analysis.
(b) Analyze the data using the Eadie–Hofstee procedure to determine K_m and R_{max}.
(c) Analyze the data using the Hanes–Wolff procedure to determine K_m and R_{max}.

CHAPTER 7

Kinetics of Reactions in the Solid State

One of the most important aspects of studying chemical dynamics is that of trying to deduce information about the mechanisms of reactions. This is an important consideration in any field of chemistry in which reactions are studied. It is no less the case for reactions involving solids, and many important industrial processes involve transformations in solids. For example, the drying of a solid product (a common process in industrial chemistry) involves the loss of water vapor from the material. In some cases, the water may actually be produced by the decomposition of a solid hydrate. Other types of processes involve the transformation of one solid phase of a compound into another with no change in composition. Because of some of the difficulties involved in studying reactions in solids, kinetic studies on solid state reactions has been a somewhat neglected area of chemical kinetics. However, there are some unusual aspects of solid state reactions that deserve special attention, and many of these factors will be discussed. In this chapter, we will present an overview of this growing and economically important field.

7.1 SOME GENERAL CONSIDERATIONS

Because of the topics emphasized in the study of chemistry, our thinking about reactions is conditioned by the events that occur in gas phase or solution phase reactions. For example, we are accustomed to thinking about a rate law that involves concentration of a reactant raised to some appropriate power, the order of the reaction with respect to that component. The rate of a reaction in solution or the gas phase is expressed in terms

of the change in concentration of some reactant or product with time. Thus, for

$$A \rightarrow B \tag{7.1}$$

we can write a rate law as

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} \tag{7.2}$$

If the reaction is first-order in A, the rate law can be written as

$$\text{Rate} = -\frac{d[A]}{dt} = k[A] \tag{7.3}$$

where k is the reaction rate constant. If the rate constant follows Arrhenius behavior, we know that

$$k = Ae^{-E_a/RT} \tag{7.4}$$

In this case, A is the pre-exponential (or frequency) factor, E_a is the activation energy, and T is the temperature (K). Plotting ln k versus 1/T gives a straight line that has a slope that is equal to $-E_a/RT$ and an intercept of ln A. This interpretation of the rate constant is based on the idea that a transition state is populated according to a Boltzmann distribution. However, as we shall see, this is not necessarily the case for reactions in solids. In fact, it is not at all uncommon for there to be no actual "transition state" involving altered molecules, and the energy barrier for the reaction may be related to the diffusion or advance of the product phase. In fact, it is generally true that for reactions in solids the activation energy can *not* be interpreted in terms of bond breaking and bond making as is the case for reactions in gases or solutions. Frequently, the "activation energy" (which is still based on the relationship between the rate and temperature) is related to some other process that may be of a physical nature.

As a general form, we can write a rate law as

$$-\frac{d[\text{conc}]}{dt} = k\,f[\text{react}] \tag{7.5}$$

where [react] is the concentration of a reactant and f[react] is some function of the concentration of this species. The concept of "order" is related to the molecularity of the reaction, which is the number of molecules forming the transition state. The mathematical treatment of such rate laws constitutes the subject of several earlier chapters in this book. However, the concept of molecularity has little to do with how a reaction occurs in a solid.

Reactions of materials in the solid state are strongly influenced by an enormous range of variables, and a complete treatment of this vast subject is beyond the scope of this book or, in fact, any single volume. One factor that becomes apparent immediately when dealing with solid state reactions is that the rate can generally *not* be expressed in terms of *concentrations*. We can illustrate this by means of the following example. The first step in the decomposition of metal oxalates when they are heated normally leads to the loss of carbon monoxide and the formation of a carbonate. In the case of NiC_2O_4, the process can be shown as

$$NiC_2O_4(s) \rightarrow NiCO_3(s) + CO(g) \tag{7.6}$$

The density of NiC_2O_4 is 2.235 g/cm^3. Accordingly, the "concentration" can be calculated as (2.235 g/cm^3 × 1000 cm^3/146.7 g/mol), which gives 15.23 **M**. However, *any* particle of NiC_2O_4 has the same density and, hence, the same concentration. Thus, even if the particle undergoes a change in size, its concentration does not change. In general, the concentration of a solid in moles per liter, **M**, is

$$\mathbf{M} = \frac{1000d}{\mathrm{M}} \tag{7.7}$$

with d being the density in g/cm^3 and M being the formula weight or molar mass (g/mol). For a particular solid phase, the concentration does not change even as the particle reacts. The product phase represents an advancing phase boundary into the reactant phase, but the "concentration" of the reactant phase remains constant. It is well known, however, that the reactivity of a solid depends markedly on the configuration of the solid particles in some cases. Clearly, a property other than concentration is needed to express the rate of a reaction in the solid state.

As we have mentioned earlier, the activation energy is obtained from the temperature dependence of the rate constant. For solid state reactions, there may not be a transition state that is populated according to the Boltzmann distribution law. As we consider a few types of solid state reactions, we will see that there is no simple interpretation of k possible in some instances.

In a case where a gas reacts with a solid, such as tarnishing of a metal surface, the diffusion coefficient of the gas through the product layer determines the rate of the reaction. In other cases, it may be the rate of diffusion of the metal through a product layer of metal oxide that determines the rate of reaction. As the product layer gets thicker, the rate of the reaction decreases. A kinetic study of this process determines the activation energy for a *diffusion* process. It is generally not possible to attach the usual

significance to the activation energy in terms of bond-breaking processes. For a reaction such as

$$AgCl(s) + Cu(s) \rightarrow Ag(s) + CuCl(s) \tag{7.8}$$

which can be studied by means of electrical conductivity, the temperature dependence of the rate gives a measure of the temperature effect on the conductivity of the products. These cases show that while a graph of the logarithm of the rate versus $1/T$ may be linear, the "activation energy" that results is likely to be for some process other than breaking bonds or changing molecular structure. The study of reactions in the solid state kinetically involves a considerable amount of reorientation!

Because we cannot represent the reaction rate in terms of concentrations, we must use some other approach. For reactions in the solid state, the fraction of the sample reacted, α, is frequently chosen as the reaction variable. Other possibilities include the thickness of the product layer, weight of product, or moles of product. It should be apparent that if α is the fraction of the sample *reacted*, $(1 - \alpha)$ is the fraction of the sample that has not reacted. As was shown in earlier chapters, rate laws frequently are written in a form such as $-d[A]/dt$ where [A] is the concentration of A that remains after some period of reaction, *t*. In an analogous way, many rate laws for reactions in the solid state are written in terms of $(1 - \alpha)$, which is the fraction of the sample remaining. The rate of the reaction may be expressed as being equal to $d\alpha/dt$, and the reaction has gone to completion when $\alpha = 1$. If we examine the behavior of α as a function of time for many reactions in the solid state, the general relationship can be shown as in Figure 7.1.

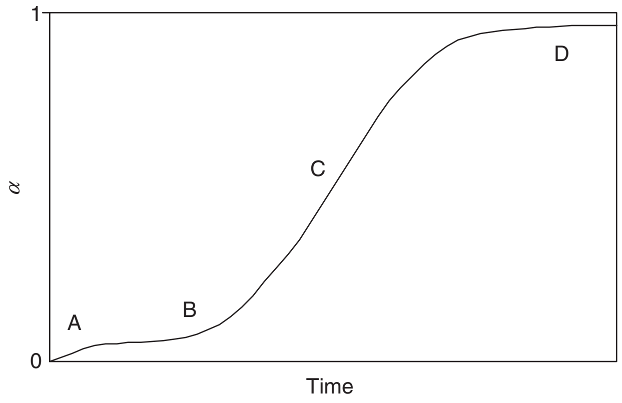


FIGURE 7.1 A general α versus time plot for a reaction in the solid state.

The curve shown in Figure 7.1 has four distinct regions that will now be described. For many reactions that can be characterized by the general equation

$$\text{Reactant}(s) \rightarrow \text{Product}(s) + \text{Gas}(g) \tag{7.9}$$

the most convenient way to determine the extent of reaction is by mass loss. It should be kept in mind that many (probably the great majority) reactions in solids must be induced by the application of some form of energy. As a result, these processes are often carried out at elevated temperatures or by absorption of electromagnetic radiation.

Let us assume for the moment that mass loss is the technique being used to follow the progress of this reaction. The region of the curve labeled as A represents the rapid evolution of adsorbed gases from the sample, which results in a small mass loss. Many solids have an affinity for one or more gases, so this is a rather common feature. Region B represents an induction period where the rate is beginning to accelerate. The region of the curve represented as C corresponds to the part of the reaction where it is progressing at the maximum rate. For most reactions in the gas phase or in solution, the initial rate is the maximum rate because that is the time when the concentration of the reactant is highest. However, many reactions in solids do not begin at the maximum rate. The reaction may proceed from particular sites (usually referred to as *active sites* or *nuclei*), and these may require some time to become fully developed. Region D is called the *decay region*, and it represents a stage where the reaction is starting to slow down markedly as the reaction approaches completion.

Although the curve shown in Figure 7.1 illustrates several different stages for a reaction of a solid, many reactions may not show all of the steps. In fact, the majority of solid state reactions do not show the desorption of gas, and although induction periods are fairly common, they are by no means universal. Consequently, it is frequently observed that the reaction starts out at the maximum rate and then the rate decreases thereafter, just as it does for reactions in the gas phase or in solutions. A reaction that takes place in the solid phase may never actually progress to $\alpha = 1$ for several reasons. First, the retention of a gaseous product in the reactant or solid product can occur. *Retention* is regarded as the adsorption (or chemisorption) of a volatile product by the solid. Because of the nature of the forces between particles that make up the solid (depending on the solid, they may be atoms, molecules, or ions), there is a tendency for a given amount of material to be arranged so as to give a minimum surface area. When heated, particles in a solid become more mobile and may rearrange to give a smaller surface area by forming rounded

corners and edges. This process, known as *sintering*, tends to increase the likelihood of retention of volatile products because the surface area becomes smaller thus hindering the escape of a volatile product. Also, cracks, pores, and other imperfections in the crystal tend to be annealed out to produce a more compact and regular structure, which also hinders the escape of a gas. The coalescence of particles due to sintering is not a factor in all reactions involving solids, but it may be important in certain cases.

With all of the features that may be exhibited in a reaction of a solid, it should not be surprising that it is frequently observed that no one rate law will describe the entire course of the reaction. Furthermore, it should come as no surprise to find that the rate laws often appear to have mathematical forms that are quite different from those that successfully describe gas and solution phase reactions. Although a large body of information and well-established principles exist, the study of reactions in solids is still largely an empirical science. Common features between reactions are often found, but many reactions in solids are often highly individualistic.

7.2 FACTORS AFFECTING REACTIONS IN SOLIDS

Because of the nature of reactions in the solid state, it is readily apparent that there are numerous factors that determine the reactivity of a particular sample. For example, if the reaction takes place on the surface of the solid, the particle size may be important because the smaller the particles, the larger the surface area for a given volume of material. The physical characteristics of the surface itself are important because the reactivity may be determined by imperfections. In a solid that is reacting, there is an interface between the reactant and product that is referred to as the *topochemistry* of the reaction. This term is analogous to describing the surface of the earth (topography) by means of a topographic map. In some instances it is possible to observe the advancing phase boundary as the reaction proceeds by appropriate microscopic techniques.

Reactions of solids frequently depend on the formation and growth of active sites called *nuclei*. For some of the kinetic models, the geometric nature of the growth of these nuclei determines the form of the rate law for the reaction. For example, a nucleus that grows in two dimensions gives rise to a different rate law than one that is growing in one or three dimensions.

From what has already been said, we can see that phase boundary advancement from these nuclei is another important factor in reactions in

solids. It should be apparent that the rate of diffusion of material may play an important role in the behavior of the reaction. Lattice defects are also important because these defects promote diffusion of material and reactivity in general because they represent high-energy centers in the solid. It has been observed that the reactivity of some solids increases dramatically in the temperature range where a phase transition occurs. This phenomenon is known as the *Hedvall effect*. Presumably, this is because at that temperature, the solid undergoes some type of crystal rearrangement. The mobility of lattice members at that temperature can promote reactivity in processes other than just the rearrangement.

Finally, the history of the sample up to the time when the reaction is studied may influence the reactivity of the solid. The treatment of the sample may cause surface damage, cracks, pores, etc., which can alter the rate of a reaction of the sample. It is also possible to heat a sample to a temperature below that at which it undergoes reaction but which is sufficient to cause some annealing to occur. This process can remove part of the defects and thereby lower the subsequent reactivity of the solid. If a solid is prepared at high temperature, slow cooling of the material allows lattice members to migrate to the positions that give a highly regular structure that is substantially free of defects. However, if the sample is prepared at high temperature and quickly quenched, there will be defects that are "quenched in" because the crystal will not have opportunity to reorient as it might have during slow cooling. All of these factors need to be considered and in some cases controlled in order to characterize fully a particular solid state process. They are also factors that make knowing all of the details of a solid state reaction very unlikely. One may have to be content with understanding a solid state process at a level that makes it possible to achieve desired goals in terms of producing a product and purifying it without knowing details about the process.

7.3 RATE LAWS FOR REACTIONS IN SOLIDS

There are approximately 20 rate laws that have been found to provide the kinetic description of reactions in the solid state. These rate laws have widely differing mathematical forms, and they are derived starting with certain models. Some of the most important rate laws will now be described and derivations shown to illustrate how the principles are applied. After doing this, we will show how the models are applied by considering a few case studies.

7.3.1 The Parabolic Rate Law

If we consider the reaction of oxygen with a solid (such as in the oxidation of the surface of a metal), the oxide layer on the surface thickens as the reaction proceeds. The rate of the reaction can be described in terms of the thickness of the layer, x, by the rate law

$$Rate = \frac{dx}{dt} \tag{7.10}$$

However, as x increases, the rate of the reaction decreases because the oxygen must diffuse through the layer of metal oxide. Therefore, the rate is proportional to $1/x$, so the rate law becomes

$$\frac{dx}{dt} = k\frac{1}{x} \tag{7.11}$$

Therefore, we can write

$$x\,dx = k\,dt \tag{7.12}$$

This equation can be integrated between the limits of $x = 0$ at $t = 0$ and some other thickness, x, at a later time, t. The result after integration can be written as

$$\frac{x^2}{2} = kt \tag{7.13}$$

or

$$x^2 = 2kt \tag{7.14}$$

After solving for x, the rate law becomes

$$x = (2kt)^{1/2} \tag{7.15}$$

Because this equation has the form of an equation for a parabola, this rate law is referred to as the *parabolic rate law*. It is interesting to examine the units on k for this case. If the thickness of the product layer is measured in cm and the time is in sec, $k = \text{cm}^2/\text{sec}$. If we consider the weight of the product layer expressed in g/cm^2, then $k = \text{g}^2\text{cm}^{-4}\,\text{sec}^{-1}$. We can also express the amount of the product layer in terms of mol/cm^2, which would lead to the units $k = \text{mol}^2\text{cm}^{-4}\,\text{sec}^{-1}$ in that case. Reactions between gases and the surfaces of solids often follow the parabolic rate law.

7.3.2 The First-Order Rate Law

Let us consider a reaction that produces a gas, G, as the reactant, R, is transformed into the product, P. The equation can be written as

$$\mathrm{R}(s) \rightarrow \mathrm{P}(s) + \mathrm{G}(g) \tag{7.16}$$

We will represent the amount of reactant R by W, the weight of the material. If the reaction follows a first-order rate law,

$$-\frac{dW}{dt} = kW \tag{7.17}$$

If W_o represents the amount of reactant initially present and W represents the amount at some later time, the integrated rate law is

$$\ln\frac{W_o}{W} = kt \tag{7.18}$$

However, the *fraction* reacted, α, is given by the amount reacted $(W_o - W)$ divided by the amount of reactant initially present, W_o.

$$\alpha = \frac{W_o - W}{W_o} = 1 - \frac{W}{W_o} \tag{7.19}$$

From this equation, we see that $-W/W_o = \alpha - 1$, so that $W/W_o = 1 - \alpha$. Substituting this result in Eq. (7.18) we obtain

$$-\ln(1-\alpha) = kt \tag{7.20}$$

The form of Eq. (7.20) shows that a plot of $-\ln(1-\alpha)$ versus t would be linear with a slope of k and an intercept of zero. Although this intercept will be observed if the reaction starts with its maximum rate, that is not always the case. For example, from Figure 7.1 we see that some reactions exhibit an induction period. If the reaction has an induction period, the first-order rate law does not represent the early stages of the reaction. The first-order rate law also does not take into account any early stage in which adsorbed gas is lost. In fact, it actually represents the portion beginning at the inflection point C in Figure 7.1 and even then may not fit the latter stages of the reaction for reasons discussed earlier. Therefore, a more general form of the first-order rate law can be written as

$$-\ln(1-\alpha) = kt + C \tag{7.21}$$

where C is a constant that represents the non-zero intercept.

Because the first-order rate law applies to cases in which the initial rate is the maximum rate, the curves that show α versus time have a *decreasing* slope throughout. Therefore, they are *deceleratory* in character because the rate of the reaction decreases. This type of behavior is also exhibited by other rate laws that are based on the concept of reaction order (second, third, etc.).

7.3.3 The Contracting Sphere Rate Law

We have described some of the difficulties that accompany kinetic interpretations of solid state reactions. In spite of this, a number of models can be described that essentially represent trial efforts for interpreting experimental results. We can expect, however, that detailed knowledge of a particular reaction is likely to be specific to that reaction. Having described the parabolic and first-order rate laws, we now consider some geometrical models. In the first of these models, we will derive the rate law for the reaction of spherical particles.

Suppose that a reaction involving a spherical solid particle of radius r takes place on the surface of the particle. Actually, it does not matter whether it is a single particle or a collection of particles of spherical shape. For this particle, the volume is given by

$$V = \frac{4}{3}\pi r^3 \tag{7.22}$$

and the surface area is given by

$$S = 4\pi r^2 \tag{7.23}$$

If the reaction takes place on the surface of the sphere, the rate will be proportional to the surface area, S. However, if we assume a uniform density, the quantity of material present is proportional to V. As a result, the volume of the particle is decreasing with time according to

$$-\frac{dV}{dt} = k_o S = k_o(4\pi r^2) \tag{7.24}$$

where k_o is a constant. However, $r = (3V/4\pi)^{1/3}$, so that

$$-\frac{dV}{dt} = 4\pi k_o \left(\frac{3V}{4\pi}\right)^{2/3} = kV^{2/3} \tag{7.25}$$

where $k = 4k_o\pi(3/4\pi)^{2/3}$, which is a constant. We can think of k as the rate constant that not only characterizes the rate of reaction but also incorporates other information. The amount of material reacting is proportional to the volume, so this equation represents a process that involves "concentration" (actually volume) to the 2/3 power. Therefore, it is sometimes said that this is "2/3-order" rate law. It should be apparent at this point that the concept of reaction "order" is of dubious meaning for solid state reactions as is the concept of molecularity.

Another way to interpret the contracting sphere rate law is to substitute for V in terms of the radius of the particle. When this is done, we obtain

$$-\left(\frac{d(4/3)\pi r^3}{dr}\right)\left(\frac{dr}{dt}\right) = -4\pi r^2 k_o = 4\pi r^2\left(\frac{dr}{dt}\right) \tag{7.26}$$

which reduces to

$$-\frac{dr}{dt} = k_o \tag{7.27}$$

This expression is equivalent to saying that the radius of the reacting particle is decreasing at a constant rate.

From Eq. (7.25), the integrated rate law is easily obtained.

$$V_o^{1/3} - V^{1/3} = \frac{kt}{3} \tag{7.28}$$

Although this is a simple model based on geometrical characteristics, there are reactions known that are modeled by a 2/3-order rate (contracting sphere) expression.

Since the general kinetic treatment of solid state reactions cannot be made in terms of concentrations, we need to put the integrated rate law for the contracting sphere in a form containing α. In this case, the amount reacted is $V_o - V$, so

$$\alpha = \frac{V_o - V}{V_o} = 1 - \frac{V}{V_o} \tag{7.29}$$

Therefore,

$$\frac{V}{V_o} = 1 - \alpha \tag{7.30}$$

Taking the cube root of each side of this equation gives

$$\left(\frac{V}{V_o}\right)^{1/3} = (1 - \alpha)^{1/3} \tag{7.31}$$

Solving this equation for $V^{1/3}$ we obtain

$$V^{1/3} = V_o^{1/3}(1 - \alpha)^{1/3} \tag{7.32}$$

Substituting for $V^{1/3}$ in the rate law shown in Eq. (7.28) yields

$$V_o^{1/3} - V_o^{1/3}(1 - \alpha)^{1/3} = \frac{kt}{3} \tag{7.33}$$

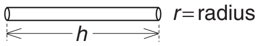
Since the initial volume of the particle, V_o, is a constant, this equation can be written as

$$1 - (1 - \alpha)^{1/3} = k't \tag{7.34}$$

where $k' = k/3V_o^{1/3} = [4k_o\pi(3/4\pi)^{2/3}]/3V_o^{1/3}$. An equation involving the function written as $1 - (1 - \alpha)^{1/3}$ also results for other cases in which a *volume* of the reacting material contracts in all three dimensions. For example, it can be shown that a cube that is reacting on the surface also leads to an equation of this general form, but the proof of that is left to the reader. A rate law of this general form is frequently referred to as a *contracting volume* rate law. The contracting volume model belongs to the deceleratory class of rate laws because the reaction rate is maximum at the beginning of the reaction when the surface area is maximum.

7.3.4 The Contracting Area Rate Law

Consider a particle of a solid that is shaped as a cylindrical rod of radius r and length h as follows.



For simplicity, we will suppose that the cylinder is very long compared to the radius, which means that $h >> r$. Therefore, the area of the ends will be considered to be insignificant compared to the area of the curved surface, and we will assume that there is no significant reaction on the ends. Consequently, we are assuming that the length remains constant during the reaction. Since the amount of material in the cylinder is represented by the volume and the reaction occurs on the surface, we can write

$$-\frac{dV}{dt} = k_o S \tag{7.35}$$

However, the surface area for the cylinder is given by

$$S = 2\pi r^2 + 2\pi rh \tag{7.36}$$

The assumption that the area of the ends of the cylinder is insignificant means that the first term on the right-hand side of this equation can be ignored and that the area can be represented as $2\pi rh$.

The volume of a cylinder is given by

$$V = \pi r^2 h \tag{7.37}$$

If we solve this equation for r, we find that

$$r = \left(\frac{V}{\pi h}\right)^{1/2} \tag{7.38}$$

Substituting for S in the rate expression shown in Eq. (7.35) followed by substitution for r gives

$$-\frac{dV}{dt} = 2\pi hk_o\left(\frac{V}{\pi h}\right)^{1/2} = 2k_o(\pi h)^{1/2}V^{1/2} \tag{7.39}$$

We can represent the quantity $2k_o(\pi h)^{1/2}$ as k and integrate from V_o at $t = 0$ to a volume of V at some later time, t.

$$\int_{V_o}^{V} \frac{dV}{V^{1/2}} = k\int_0^t dt \tag{7.40}$$

The result of the integration is

$$-2(V^{1/2} - V_o^{1/2}) = kt \tag{7.41}$$

Simplifying this equation gives the integrated rate law

$$V_o^{1/2} - V^{1/2} = \frac{kt}{2} = k't \tag{7.42}$$

Therefore, the reaction is of "$^1/_2$ -order" in terms of the volume of the material present (equivalent to concentration or amount). Note that if the reaction is followed by the change in the volume of the sample, the *measured* rate constant, k', is not the same as the *intrinsic* rate constant, k, because of geometrical constraints.

We can now determine how the radius of the cylinder will change with time. The change in volume of the cylinder can be expressed in terms of the radius as

$$-\frac{dV}{dt} = -\left(\frac{dV}{dr}\right)\left(\frac{dr}{dt}\right) = 2\pi r k_o h \tag{7.43}$$

since the volume of the cylinder is given by $\pi r^2 h$. Taking the derivative dV/dr yields

$$\frac{dV}{dr} = 2\pi r h \tag{7.44}$$

Therefore, substituting this result in Eq. (7.43) gives

$$-2\pi r h\frac{dr}{dt} = 2\pi r h k_o \tag{7.45}$$

Solving for dr/dt yields

$$\frac{dr}{dt} = k_o \tag{7.46}$$

This result indicates that the radius of the cylindrical particle decreases at a constant rate, exactly as it did in the contracting sphere model considered earlier. It is interesting to note that the contracting sphere gave a rate law that was "2/3-order," and the present case, assuming that one dimension (the length) remains constant, gives a "1/2-order" rate law. Thus, shrinking of the particle in *three* dimensions leads to "2/3-order," while shrinking the particle in *two* dimensions leads to "1/2-order." These are general observations that are followed for particles having other geometrical structures.

The integrated rate equation can be expressed in terms of α, the fraction reacted, because

$$\alpha = \frac{V_o - V}{V_o} \tag{7.47}$$

Therefore,

$$\frac{V}{V_o} = 1 - \alpha \tag{7.48}$$

Taking the square root of both sides of this equation gives

$$\left(\frac{V}{V_o}\right)^{1/2} = (1 - \alpha)^{1/2} \tag{7.49}$$

Solving for $V^{1/2}$ we obtain

$$V^{1/2} = V_o^{1/2}(1 - \alpha)^{1/2} \tag{7.50}$$

Substituting this value for $V^{1/2}$ into Eq. (7.42), we obtain

$$V_o^{1/2} - V_o^{1/2}(1 - \alpha)^{1/2} = \frac{kt}{2} = V_o^{1/2}[1 - (1 - \alpha)^{1/2}] \tag{7.51}$$

where $k' = k/2V_o^{1/2}$. Therefore, the rate law can be simplified to give

$$1 - (1 - \alpha)^{1/2} = \frac{kt}{2V_o^{1/2}} = k't \tag{7.52}$$

The rate law for the contracting area shows that a plot of $1 - (1 - \alpha)^{1/2}$ versus time will lead to a straight line if the reaction follows a "1/2-order" rate law. This is another of the deceleratory rate laws.

A few words are in order at this point concerning the apparent rate constant. If a plot is made of $1 - (1 - \alpha)^{1/2}$ versus time and a straight line is obtained, the slope of that line will enable a calculation of k' to be made. If the reaction is subsequently carried out at several temperatures, an Arrhenius plot can be made and an activation energy can be determined. This is assuming, of course, that the rate constant follows Arrhenius behavior, an assumption that cannot always be made for solid state reactions. However, the rate constant k' has incorporated in it other factors related to the geometry of the system. For this case, $k' = k/2V_o^{1/2}$ and $k = 2k_o(\pi h)^{1/2}$. Therefore, because the *measured* rate constant is not that expressed in the original differential rate law, the line that results from the Arrhenius plot will be displaced upward or downward by a constant amount. While this does not affect the value of the activation energy calculated from the *slope* of the line, it *does* affect the intercept. Therefore, the Arrhenius plot cannot be used directly to determine the pre-exponential factor from the intercept.

7.4 THE PROUT–TOMPKINS EQUATION

In Chapter 2, the effect of a product of a reaction functioning as a catalyst was examined. It was shown that this type of behavior resulted in a concentration versus time curve that is sigmoidal in shape. It appears that there is autocatalysis in the early stages of some reactions in the solid state,

which is usually more important in the acceleratory period of the reaction. An equation for autocatalysis has the form (see Section 2.6)

$$\ln\frac{\alpha}{1-\alpha} = kt + C \tag{7.53}$$

This equation is based on a homogeneous reaction where the product can catalyze the reaction of particles of the reactant. The derivation presented here for this equation follows closely that presented by Young (1966).

If N_o is the number of nuclei present at the beginning of the reaction, the change in number of nuclei with time, dN/dt, can be expressed as

$$\frac{dN}{dt} = k_o N_o + k_1 N - k_2 N \tag{7.54}$$

The first two terms on the right-hand side of Eq. (7.54) give the number of nuclei originally present and the number of nuclei produced by branching (which can be thought of as some of the N_o nuclei spawning new nuclei). The last term expresses the loss of nuclei that results when nuclei are terminated. Termination occurs when a spreading nucleus encounters product and thus cannot continue to spread as a reaction site. After the original nucleation sites are spent, Eq. (7.54) will become

$$\frac{dN}{dt} = (k_1 - k_2)N \tag{7.55}$$

For reactive sites that are linear nuclei, the fraction of the sample reacted will vary with the number of nuclei as

$$\frac{d\alpha}{dt} = kN \tag{7.56}$$

In order to arrive at a final equation that expresses α as a function of time, it is necessary to obtain a relationship between the constants in Eq. (7.55). For a *symmetrical* sigmoidal curve, there will be an inflection point, α_i, at 0.5. At the inflection point, $d\alpha/dt$ has its maximum value (the second derivative changes sign) because at that point the second derivative is equal to zero, and, therefore, at that point, $k_1 = k_2$. Therefore, at the inflection point $k_2 = k_1\alpha/\alpha_i$. Substituting this result for k_2 in Eq. (7.55) we find that

$$\frac{dN}{dt} = k_1 N - k_2 N = k_1 N - \frac{\alpha}{\alpha_i} k_1 N \tag{7.57}$$

This equation can be put in the form

$$\frac{dN}{dt} = k_1 N\left(1 - \frac{\alpha}{\alpha_i}\right) \tag{7.58}$$

By making use of Eq. (7.56), we can write N as

$$N = \frac{1}{k} \cdot \frac{d\alpha}{dt} \tag{7.59}$$

Substituting this result in Eq. (7.58), we obtain

$$\frac{dN}{dt} = \frac{k_1}{k} \cdot \frac{d\alpha}{dt}\left(1 - \frac{\alpha}{\alpha_i}\right) \tag{7.60}$$

By removing dt, we can write this equation as

$$\frac{dN}{d\alpha} = \frac{k_1}{k}\left(1 - \frac{\alpha}{\alpha_i}\right) \tag{7.61}$$

Therefore, the equation can be put into the form

$$dN = \frac{k_1}{k}\left(1 - \frac{\alpha}{\alpha_i}\right)d\alpha = \frac{k_1 d\alpha}{k} - \frac{k_1}{k} \cdot \frac{\alpha d\alpha}{\alpha_i} \tag{7.62}$$

This equation can be integrated to give the relationship between α and the number of nuclei,

$$N = \frac{k_1}{k}\alpha\left(1 - \frac{\alpha}{2\alpha_i}\right) \tag{7.63}$$

When the fraction reacted at the inflection point is 0.5, $\alpha_i = 0.5$ and

$$\frac{d\alpha}{dt} = kN = k\frac{k_1}{k}\alpha(1 - \alpha) = k_1\alpha(1 - \alpha) \tag{7.64}$$

Rearranging this equation leads to

$$d\alpha = k_1\alpha(1 - \alpha)dt \tag{7.65}$$

or

$$\frac{d\alpha}{\alpha(1 - \alpha)} = k_1 dt \tag{7.66}$$

Integration of this equation involves evaluating an integral of the form

$$\int \frac{dx}{x(ax + b)} = \frac{1}{b}\ln\frac{x}{ax + b} \tag{7.67}$$

Therefore, after integrating and simplifying the result, the rate law can be written as

$$\ln\frac{\alpha}{(1 - \alpha)} = k_1 t + C \tag{7.68}$$

which is exactly the form of the Prout–Tompkins rate law.

The Prout–Tompkins rate law describes a process that involves linear-branching chain nuclei that can be terminated when they reach the product phase. It is generally used to analyze the acceleratory portion of reactions (typically up to $\alpha = 0.3$ or so). An equation having this form was originally used by Prout and Tompkins in their study on the decomposition of potassium permanganate, and it has also been applied to the decomposition of silver oxide (Young, 1966).

7.5 RATE LAWS BASED ON NUCLEATION

Many chemical reactions in the solid state follow rate laws that are based on the process of nucleation. The active sites have been observed microscopically in some cases, and the phenomenon of nucleation is well established. Although they will not be described in detail, several other processes have nucleation as an integral part of at least the early stages. For example, crystal growth has been successfully modeled by this type of rate law. Condensation of droplets is also a process that involves nucleation. Consequently, kinetics of a wide variety of transformations obey rate laws that have some dependence on a nucleation process.

The general form of the rate law that is used to describe nucleation processes is known as the Avrami (or Avrami–Erofeev) rate law,

$$\alpha = 1 - e^{-kt^n} \tag{7.69}$$

which can be written in logarithmic form as

$$[-\ln(1-\alpha)]^{1/n} = kt \tag{7.70}$$

In this rate law, n is called the *index of reaction*, and it usually has values of 1.5, 2, 3, or 4. These rate laws are generally abbreviated as A1.5, A2, etc. In particular, the A1.5 rate law (when $n = 1.5$, $1/n$ is $2/3$, so this rate law is sometimes identified in that way) has been used to describe crystallization processes in some solids. The rate laws having $n = 2$ and $n = 3$ are associated with two- and three-dimensional growth of nuclei, respectively.

Nuclei may be present initially or they may grow in at certain locations by a process that is usually considered to be first-order. The derivation of the Avrami rate law can be accomplished by several procedures (see Young, 1966), all of them rather complicated. Therefore, a detailed derivation will not be presented nor is it needed to see the applications of this type of rate law. In general, assumptions are made regarding the rate of change in the

number of nuclei and the volume swept out by them as they react. When the volume of all the nuclei is considered along with the volume change of the nuclei as they react, it is possible to derive the equation

$$-\ln(1-\alpha) = C\left(e^{-kt} - 1 + kt - \frac{(kt)^2}{2!} + \frac{(kt)^3}{3!}\right) \tag{7.71}$$

(where C is a constant representing a collection of constants that involves, among other things, N_o). This equation is the most general form of the *random nucleation* rate law. At longer times (represented by the decay region of the α versus time curve), the term $(kt)^3/3!$ dominates, so the equation reduces to

$$-\ln(1-\alpha) = C'k't^3 \tag{7.72}$$

Taking the cube root of this equation and letting $k'' = (C'k')^{1/3}$ yields an equation of the form

$$[-\ln(1-\alpha)]^{1/3} = k''t \tag{7.73}$$

which is an Avrami rate law with an index of 3 (the A3 case). This equation shows that a plot of $[-\log(1-\alpha)]^{1/3}$ versus time should be linear.

When written in exponential form, Eq. (7.72) becomes

$$\alpha = 1 - e^{-C'k't^3}$$

It can also be shown that the early stages of the reaction sometimes follow a rate law in which α varies as t^4. The general equation

$$\alpha = 1 - e^{-kt^n} \tag{7.74}$$

can also be derived from certain geometric models that have been applied to the decomposition of crystalline hydrates (Young, 1966).

In order to provide a practical example of the type of behavior exhibited by a reaction that follows an Avrami–Erofeev rate law, the data presented in Table 7.1 were derived. In performing the calculations, it was assumed that the reaction follows an Avrami–Erofeev rate law with an index of 2 (the A2 rate law) and that k is $0.025\ \text{min}^{-1}$.

Having a set of (α,t) data available, a graph was prepared to illustrate the type of plot that can be expected when a reaction follows an Avrami–Erofeev rate law. The result is shown in Figure 7.2, and the sigmoidal curve is characteristic of a reaction that follows a nucleation rate law. In Chapter 2, it was shown that a sigmoidal rate plot results from autocatalysis, but for reactions in the solid state such plots are more likely to indicate that the reaction is controlled by some type of nucleation process.

TABLE 7.1 Values of α as a Function of Time for a Reaction Following an Avrami–Erofeev Rate Law with $n = 2$ and $k = 0.025\ \text{min}^{-1}$.

Time (min)	α	Time (min)	α
0	0.000	55	0.849
5	0.016	60	0.895
10	0.061	65	0.929
15	0.131	70	0.953
20	0.221	75	0.970
25	0.323	80	0.981
30	0.430	85	0.989
35	0.535	90	0.994
40	0.632	95	0.996
45	0.718	100	0.998
50	0.790		

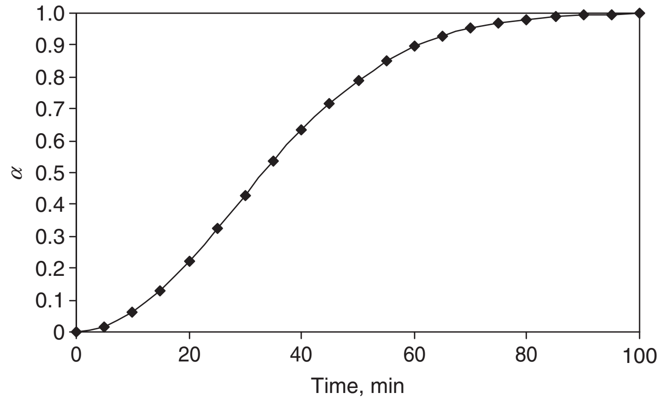


FIGURE 7.2 A plot of α versus time for the data shown in Table 7.1.

Many reactions in the solid state follow a rate law of the Avrami–Erofeev type. For example, the dehydration of $CuSO_4{\bullet}5H_2O$ is a process where the first two steps can be represented as

$$CuSO_4{\bullet}5H_2O(s) \rightarrow CuSO_4{\bullet}3H_2O(s) + 2\ H_2O(g) \quad (7.75)$$

$$CuSO_4{\bullet}3H_2O(s) \rightarrow CuSO_4{\bullet}H_2O(s) + 2\ H_2O(g) \quad (7.76)$$

These reactions take place in the range of 47 to 63°C and 70.5 to 86°C, respectively. Both reactions appear to follow an Avrami–Erofeev rate law with an index of 2 over a range of α from 0.1 to 0.9 (see Ng, et al., 1978).

For a rate law having the form $[-\ln(1-\alpha)]^{1/n} = kt$, the most obvious way to evaluate the constants n and k is to take the logarithm of both sides of the equation, which yields

$$\frac{1}{n}\ln[-\ln(1-\alpha)] = \ln(kt) = \ln k + \ln t \tag{7.77}$$

From this equation, we see that a plot of $\ln[-\ln(1-\alpha)]$ versus $\ln(t)$ should give a straight line having a slope of n and an intercept of $n[\ln(k)]$ when the correct value of n is used. In practice, it is usually preferable to plot the function $[\ln(1/(1-\alpha))]^{1/n}$ versus time in order to test various values of n. This is because the form involving the ln ln function is insensitive to small changes in the data due to the nature of that function.

7.6 APPLYING RATE LAWS

The rate laws discussed up to this point involve a large number of mathematical forms that involve functions of $(1-\alpha)$. Those shown earlier and a few others are summarized in Table 7.2. It is readily apparent that several of the rate laws have very similar mathematical forms. Consequently, applying these equations to data obtained from experiments on solid state reactions may result in more than one of the equations giving about equally good fit to the data. It is frequently the case that it is virtually impossible to determine with certainty which of the rate laws is correct if all one has to go on is the data for α as a function of time obtained from a limited number of kinetic runs. Because of the nature of solid state reactions, it is frequently impossible to follow the reaction over several half-lives as is always recommended for reactions in solution. In these cases, it is helpful to have data from several different experiments so that errors in the data (generally in the α values, since it is often difficult to determine the fraction of the sample reacted accurately) do not make it impossible to identify the correct rate law. (An example of this situation was illustrated in Section 1.3). The characteristics described above can be illustrated by the following example. Figure 7.3 was constructed using the data presented in the table.

Although the "correct" value of n is 2 in this case (the value used in calculating the data), the data were also fitted to rate laws having n values of 1.5 and 3. The resulting curves are also shown in Figure 7.3. Note that only

TABLE 7.2 Rate Laws for Reactions in Solids.

Description		Mathematical Form
Acceleratory α-time curves		
	Power law	$\alpha^{1/n}$
	Exponential law	$\ln \alpha$
Sigmoidal α-time curves		
A1.5	Avrami–Erofeev one-dimensional growth of nuclei	$[-\ln(1-\alpha)]^{2/3}$
A2	Avrami–Erofeev two-dimensional growth of nuclei	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami–Erofeev three-dimensional growth of nuclei	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/4}$
B1	Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$
Deceleratory α-time curves based on geometrical models		
R1	One-dimensional contraction	$1-(1-\alpha)^{2/3}$
R2	Contracting area	$1-(1-\alpha)^{1/2}$
R3	Contracting volume	$1-(1-\alpha)^{1/3}$
Deceleratory α-time curves based on diffusion		
D1	One-dimensional diffusion	α^2
D2	Two-dimensional diffustion	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	Three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$
D4	Ginstling–Brounshtein	$[1-(2\alpha/3)]-(1-\alpha)^{2/3}$
Deceleratory α-time curves based on reaction order		
F1	First-order	$-\ln(1-\alpha)$
F2	Second-order	$1/(1-\alpha)$
F3	Third-order	$[1/(1-\alpha)]^2$

the line on the graph corresponding to $n = 2$ is straight. Moreover, the line resulting when n was set equal to 3 is concave *downward* while that resulting when n was set equal to 1.5 is concave *upward*. It is a general characteristic of plots that test Avrami–Erofeev rate laws that if n is *larger* than the correct value, the line is curved and will be *concave downward*. Conversely, if n is *smaller* than the correct value, the line will be *concave upward*.

Another conclusion can be illustrated by studying Figure 7.3. If only a few data points were available and if they were subject to substantial errors, as they frequently are for solid state reactions, it would be difficult (if not impossible) to determine the correct index of reaction. Also, some other

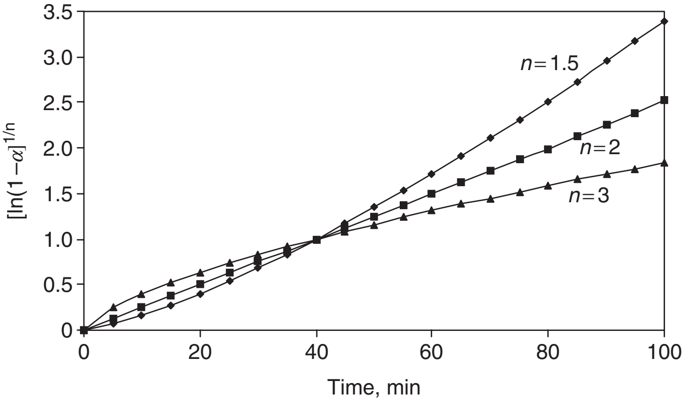


FIGURE 7.3 Avarami–Erofeev plots of the data shown in Table 7.2.

function shown in Table 7.2 might fit the data about equally well. In this example, the data were calculated assuming that $k = 0.025\,\text{min}^{-1}$ and the entire range of α values was used. If a more limited range of experimental α values is available for use in the calculations, selection of the correct rate law is not a trivial problem, especially when there are errors in the data due to experimental conditions and measurements.

As was illustrated in Chapter 1, errors in the data can make it difficult to distinguish the correct rate laws, especially when the reaction is followed only to 50 or 60% completion. For solid state reactions, it may be virtually impossible to assign a unique rate law under these conditions because of the mathematical similarity of the rate laws. The general rule for determining the rate law for a reaction in kinetic studies is to follow the reaction over several half-lives (see Chapter 1). However, this is almost never possible for a solid state reaction and even if it were, the "correct" rate law could very well be different in different stages of the reaction (see Section 7.1). Data points in the range $0.1 < \alpha < 0.9$ are generally chosen to avoid any induction period and the decay region unless these regions are specifically under study. As a result of these factors, it is generally necessary to make a rather large number of kinetic runs to try to determine a rate law that is applicable to the reaction. This will be illustrated in the next section.

In Chapter 8, it will be shown that most of the rate laws shown in Table 7.2 can be put in the form of a composite rate law involving three exponents. We will also describe the difficulties associated with attempts to determine these exponents from (α,t) data. While the discussion up to this point has set forth the basic principles of solid state reactions, their application to specific

studies has not been shown. In the next section, the results obtained from a few case studies of reactions in solids will be considered to show how they can be interpreted. In spite of the difficulties associated with studying reactions in the solid state, a great deal of insight is often possible.

7.7 RESULTS OF SOME KINETIC STUDIES

In order to prevent the development of principles of solid state kinetics from being an abstract exercise, summaries will be presented that illustrate how kinetic results have been interpreted in specific cases. Although the studies are not necessarily complete, they will show that a great deal of information about solid state reactions can be deduced from kinetic studies as long as the basic principles are understood and applied correctly.

7.7.1 The Deaquation–Anation of $[Co(NH_3)_5H_2O]Cl_3$

When aquapentamminecobalt(III) chloride and similar compounds are heated, the water is driven off and an anion replaces it in the coordination sphere of the metal. Because an *anion* is replacing a volatile ligand, this type of reaction is known as an *anation* reaction. In the case to be discussed here, the reaction is

$$[Co(NH_3)_5H_2O]Cl_3(s) \rightarrow [Co(NH_3)_5Cl]Cl_2(s) + H_2O(g) \qquad (7.78)$$

However, when other anions (e.g., Br^-, NO_3^-, or SCN^-) are present, the kinetic behavior of the reaction is altered. For example, activation energies of 79, 105, and 139 kJ/mol have been reported for the Cl^-, Br^-, and NO_3^- compounds, respectively, in an early study. This behavior, sometimes referred to as an "anion effect," has led various workers to postulate a mechanism like that shown in Scheme I.

Scheme I

$$[Co(NH_3)_5H_2O]Cl_3 \overset{\text{slow}}{\rightleftharpoons} [Co(NH_3)_5H_2OCl]Cl_2 \qquad (7.79)$$

$$[Co(NH_3)_5H_2OCl]Cl_2 \xrightarrow{\text{fast}} [Co(NH_3)_5Cl]Cl_2 + H_2O \qquad (7.80)$$

In this mechanism, the slow step involves an anion leaving a lattice site and entering the coordination sphere of the metal to give a seven-bonded

transition state. Because both the $[Co(NH_3)_5H_2O]^{3+}$ cation and the Cl^- anion are involved in forming the transition state, the process has been referred to as S_N2. However, the compound already contains three chloride ions per cation, and the formula $[Co(NH_3)_5H_2O]Cl_3$ contains *both* cation and anions. Therefore, it is not clear what S_N2 means when only the compound $[Co(NH_3)_5H_2O]Cl_3$ is the reactant.

A mechanism like that just described is very unlikely on the basis of energetics. First, a negative ion must leave an anion site in the lattice which would form a Schottky defect (an ion missing from a lattice site), which is a high-energy process. Second, the anion must attach to the $[Co(NH_3)_5H_2O]^{3+}$ cation to produce a 7-bonded transition state. Such complexes require sacrificing a considerable amount of energy in the form of the crystal field stabilization energy. As a result of these processes, it can be shown that the activation energy for this reaction would be much larger than the 79 kJ/mol reported for the deaquation-anation reaction of the chloride compound.

A more realistic approach to the mechanism of this reaction is that water is lost from the coordination sphere of the metal and that it must occupy interstitial positions in the crystal lattice. This process can be considered to be the formation of a defect followed by diffusion of the volatile product through the lattice (the *defect-diffusion* mechanism). Diffusion of H_2O through the lattice is favored by the cation and anion having greatly differing sizes because the fraction of free space increases as the difference in size of the cation and anion increases. Therefore, since the cation is large, water should escape most easily from the chloride compound. Thus, the activation energy should vary with the size of the anion $Cl^- < Br^- < I^-$, and in a later study the reported activation energies are 110.5, 124.3, and 136.8 kJ/mol, respectively, for these anions.

Part of the misconception regarding the kinetics of the deaquation-anation reaction stems from the fact that only a limited analysis of the data was performed. To be complete, the data should be analyzed using all of the rate laws shown in Table 7.2. A more recent study of this process by Hamilton and House was completed in which the reaction was studied by means of mass loss as the H_2O is driven off. Figure 7.4 shows typical rate plots that were obtained for the process when carried out at several constant temperatures.

When the data are presented in this way, the unmistakable sigmoidal nature of the rate plots for dequation-anation of $[Co(NH_3)_5H_2O]Cl_3$ suggests that the process obeys an Avrami–Erofeev type of rate law. In

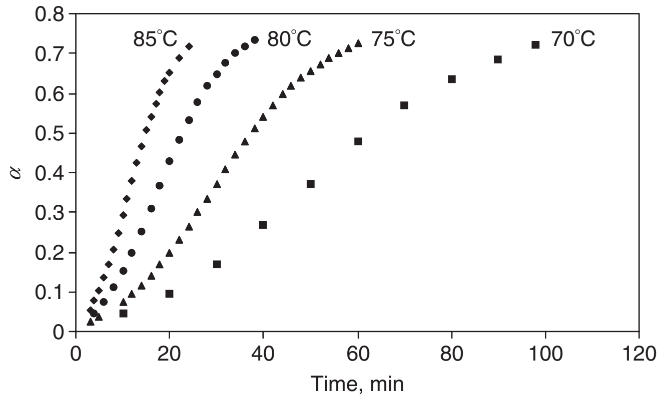


FIGURE 7.4 Rate plots for the dehydration-anation reaction of $[Co(NH_3)_5H_2O]Cl_3$.

order to test the rate laws, several runs were carried out at each temperature. When the data from a total of 32 reactions (involving four temperatures) were analyzed by means of a computer technique that tests all of the rate laws shown in Table 7.2, it was found that 26 of the runs gave the best fit with the A1.5 rate law, 4 gave the best fit with the A2 rate law, and 2 gave the best fit with the R3 (contracting volume) rate law. Not a single run gave the best fit to the data with a first- or second-order rate law.

An A1.5 rate law is one form of a nucleation rate law, and it has also been shown to represent a diffusion process. The rate constants obtained when using the A1.5 rate law,

$$[-\ln(1-\alpha)]^{2/3} = kt \tag{7.81}$$

to represent the (α,t) data were used to prepare the Arrhenius plot shown in Figure 7.5.

The slope of the line corresponds to an activation energy of 97 kJ/mol, which is a somewhat different value than the value of 79 kJ/mol reported by others in the earlier studies. However, the earlier results were obtained with assumptions about the rate law that do not appear to be valid.

This study serves to illustrate how the application of kinetic labels such as S_N1 or S_N2 for reactions in solids can be misleading. Only by careful analysis of data from a large number of runs using a wide range of rate laws can a correct modeling of a reaction be obtained. Unfortunately, this fact has been overlooked many times in the past by workers who have assumed that the kinetics of reactions in the solid state and in solution should be similar. It should be pointed out that since this initial application

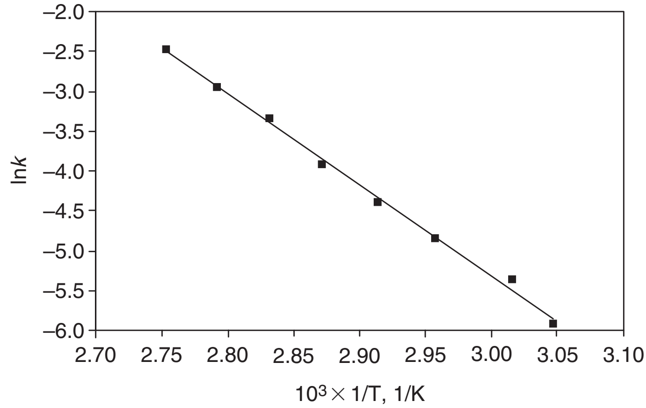


FIGURE 7.5 Arrhenius plot for the dehydration-anation reaction of $[Co(NH_3)_5H_2O]Cl_3$ when the Avrami–Erofeev rate law with $n = 1.5$ is used.

of the defect-diffusion mechanism, it has been shown that many other reactions have kinetic features that are consistent with this mechanism.

7.7.2 The Deaquation-Anation of $[Cr(NH_3)_5H_2O]Br_3$

The deaquation-anation reaction of $[Cr(NH_3)_5H_2O]Br_3$,

$$[Cr(NH_3)_5H_2O]Br_3(s) \longrightarrow [C_r(NH_3)_5Br]Br_2(s) + H_2O(g) \qquad (7.82)$$

illustrates some of the classic problems associated with the study of reactions in the solid state (Ingram, 1995). When the (α,t) data for this reaction were tested by fitting the data to the rate laws shown in Table 7.2, none of the rate laws gave an especially good fit over a wide range of α values. The sigmoidal shape of the curves showing α as a function of time suggested that an Avrami type of rate law should be applicable. In this case, the (α,t) data for each run were divided into two groups. The first group consisted of data with $0.1 < \alpha < 0.5$, while the second group consisted of data for which $0.5 < \alpha < 0.9$. In this way, an attempt was made to identify rate laws that would be applicable to certain regions of the reaction rather than trying to fit a single rate law to the entire process.

Four reactions were carried out at each of the temperatures 85, 90, 95, 100, 105, and 110°C. From analysis of the data for the portion of the reactions where α was in the range 0.1 to 0.5, 20 out of the 24 sets of data gave the best fit with the A2: $[-\ln(1-\alpha)]^{1/2}$ rate law. On the other hand, when α was in the range of 0.5 to 0.9, all 24 sets of (α,t) data gave the best fit with the D3: $[1-(1-\alpha)^{1/3}]^2$ (three-dimensional diffusion)

rate law. In every case, the correlation coefficient was at least 0.9999, showing that the rate law fit the data extremely well.

These results show that in the early part of the reaction the rate of the reaction is controlled by the formation of nuclei that grow in two dimensions (the A2 rate law). In the latter stage, the rate of the reaction is controlled by diffusion of water through the lattice. Such results are in accord with the defect-diffusion model that is described in Section 7.7.1. It seems likely in this case that the early loss of water is from near the surface of the particles as the process of nucleation occurs. The later stages of the reaction involve the loss of water from the interior of the crystals and thus are controlled by the rate of diffusion of water to the surface. It is particularly important to note that for this reaction none of the rate laws gave a good fit to the data over a wide range of α values. However, the data are very well correlated by two different rate laws that apply to different portions of the reaction. This underscores the fact that in some cases no single rate law models the entire reaction.

The kinetics and mechanism of this reaction serve to show that even a comparatively simple-looking reaction in the solid state may exhibit peculiarities that make it quite different from other reactions that otherwise appear similar. Of course, the reactions of H_2 with I_2 and with Cl_2 that were described in Chapter 1 show that this is by no means restricted to reactions in solids.

7.7.3 The Dehydration of *Trans*-$[Co(NH_3)_4Cl_2]IO_3{\bullet}2H_2O$

When solid *trans*-$[Co(NH_3)_4Cl_2]IO_3{\bullet}2H_2O$ is heated, it loses the water of hydration and simultaneously isomerizes to *cis*-$[Co(NH_3)_4Cl_2]IO_3$. An early study of this reaction indicated that it follows the rate law

$$-\ln(1-\alpha) = kt + c \tag{7.83}$$

However a later study showed that when the material was heated in thin beds in a nitrogen atmosphere, the reaction was described by the rate law

$$-\ln(1-\alpha) = kt^2 + c \tag{7.84}$$

In the same study, it was reported that the reaction followed a first-order rate law when the sample was arranged in thick beds. Also, the activation energy was reported to vary from 58 kJ/mol when the static nitrogen pressure was 0.1 torr to 116 kJ/mol when the nitrogen pressure was

650 torr. In a flowing nitrogen atmosphere, an activation energy of 57 kJ/mol was found.

A more recent study of this reaction was conducted to try to determine some of the kinetic features. In this study, the kinetics of the reaction involved using samples of *trans*-$[Co(NH_3)_4Cl_2]IO_3{\bullet}2H_2O$ having a particle size distribution of 57 $\pm$ 15 pm (House and Eveland, 1994). The reaction was carried out in the range of temperature from 120 to 140°C, and the (α,t) data were analyzed by testing with all of the rate laws shown in Table 7.2. Figure 7.6 shows the rate plots obtained when data in the range $0.1 < \alpha < 0.8$ were analyzed.

From the rate plots shown in Figure 7.6, it is readily apparent that the reaction should follow a rate law that is one of the deceleratory types. This suggests that the reaction could obey an order, diffusion-controlled, or geometric type of rate law. Four runs were made at each temperature (120, 125, 130, 135, and 140°C), so data were available from a total of 20 runs. When the data were fitted to all of the rate laws shown in Table 7.2, 12 out of the 20 data sets gave the best fit with the second-order rate law

$$\frac{1}{1-\alpha} = kt \tag{7.85}$$

The data from the other eight reactions all gave the best fit with the third-order rate law,

$$\frac{1}{(1-\alpha)^2} = kt \tag{7.86}$$

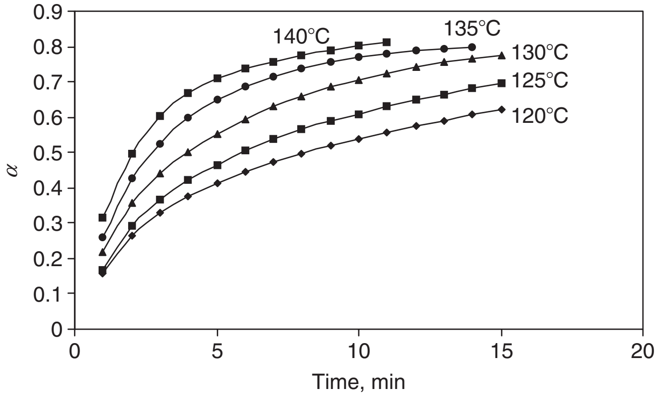


FIGURE 7.6 Rate plots for the dehydration of *trans*-$[Co(NH_3)_4Cl_2]IO_3{\bullet}2H_2O$.

Using the rate constants obtained by application of the second-order rate law, an Arrhenius plot yielded an activation energy of 103 kJ/mol, which is not much different from the value of 116 kJ/mol reported by other workers when the reaction was carried out under nitrogen at a pressure of approximately 1 atm.

In order to further investigate the details of this interesting reaction, the early portion represented by $0.1 < \alpha < 0.3$ and an intermediate portion for which $0.3 < \alpha < 0.5$ were considered. In each case, these regions of the curves were greatly expanded in order to provide at least 20 data points in each portion of the curves. This could be done because the reaction was followed by thermogravimetric analysis (see Chapter 8), which made it possible to determine the mass loss at very small time intervals. Data from these smaller portions of the curves were tested using a computer program that fits the data to all of the rate laws shown in Table 7.2. The reaction at 140°C was so rapid that the range with $0.1 < \alpha < 0.3$ could not be analyzed accurately. Therefore, data from only 16 runs were analyzed in that region, and 10 of these gave data that provided the best fit with the third-order (F3) rate law. The data from the other six runs gave the best fit with diffusion control rate laws, D4 (2 runs), D2 (3 runs), and D1 (1 run). An F3 rate law does not indicate a molecularity of three for the transition state, but it probably indicates that the initial loss of water is very rapid when $\alpha < 0.3$, and the data simply happen to fit that mathematical function as the water is flashed off quickly. An activation energy of 80 kJ/mol was found for loss of water in the early portion of the reaction.

From the analysis of the (α,t) data for the portion of the reaction represented by the interval $0.3 < \alpha < 0.5$, it was found that only 2 of the 20 runs gave the best fit with the F3 rate law. The remaining 18 runs gave data that were best correlated by the diffusion control rate laws. The results were D3 (7 runs), D2 (6 runs), D1 (3 runs), and D4 (2 runs). Although results such as these may be somewhat disquieting, this situation is not unusual. Fitting the data to the rate laws by numerical analysis often involves data points that have only small differences in values. It is quite possible that more than one function can be used to approximate the data with only very slight differences in correlation coefficients.

Although there is little doubt that the reaction in the $0.3 < \alpha < 0.5$ region follows a rate law indicating diffusion control, it is not clear whether the D3 or D2 rate law is the correct one, but there is a slight preference for the D3. Using the rate constants calculated assuming that the D3 rate law is correct, an activation energy of 110 kJ/mol is obtained. Certainly the rate

of loss of water from the interior of the crystalline solid could well be expected to be controlled by diffusion, of either two- or three-dimensional character.

The fact that the overall process appears to follow an F2 rate law is probably a compromise between different stages that follow other rate laws, even though correlation coefficients in the 0.998 to 0.999 range were found. This study points out that even a material having a rather homogeneous particle size distribution studied in a highly replicated manner can yield less than complete agreement as to the applicable rate law. It also shows that the study of different regions of a reaction can yield valuable insight as to changes in the mechanism as the reaction progresses. As stated earlier in this chapter, it is unlikely that a single rate law will describe the entire reaction, but such is the nature of solid state reactions.

7.7.4 Two Reacting Solids

Under certain conditions, particles of two different types of solid materials may react. This can be as a result of a more favorable match of character according to the hard-soft interaction principle. In order to make the structural units (usually ions) mobile, some energy source is normally applied. The most common way to bring about the reaction between two solids is by heating them in close contact. The application of pressure may also provide added inducement for the reaction to occur.

A more unusual way to cause particles of solids to react is by the application of ultrasound. When a pulse of ultrasound is sent out into a liquid, it causes cavitation within the liquid. However, with internal pressures in the range of 2000–8000 atm, the cavities implode violently. If particles of the solids are suspended in the liquid, they will be driven together with energies that are sufficient to cause a reaction to take place. In addition to the kinetic energy imparted to the particles, there is also instantaneous heating to very high temperatures.

The question arises as to what type of rate law can be used to model reactions between two solids. Probably the most widely employed rate law is that known as the Jander equation,

$$\left[1-\left(\frac{100-y}{100}\right)^{1/3}\right]^2 = kt \tag{7.87}$$

where y is the percent reacted (percent completion). This is essentially the same as three-dimensional diffusion, which can be easily seen when the Jander equation is written as

$$\left[1-\left(1-\frac{y}{100}\right)^{1/3}\right]^2 = kt \tag{7.88}$$

If y is the percent reacted, $y/100$ is the fraction reacted, α, so this equation is analogous to the three-dimensional diffusion rate law,

$$[1-(1-\alpha)^{1/3}]^2 = kt \tag{7.89}$$

Although causing a reaction between two solids by heating them is a common practice, a reaction between two solids using ultrasound as the energy source was studied by Kassel (1994). This work was carried out to assess the feasibility using this technique as a basis for kinetic studies. One reaction studied was

$$CdI_2 + Na_2S \xrightarrow{\text{ultrasound}} CdS + 2\ NaI \tag{7.90}$$

The solids were suspended in dodecane, and the mixture was sonicated using a pulsed source. At specific times, samples of the solids were separated from the reaction mixture and analyzed to determine the amount of CdS formed. The extent of reaction was found to vary with sonication time, although the data showed considerable scatter. Although the results did not represent a highly sophisticated kinetic study, they indicated that the Jander equation represents a rate law that should be considered when a model for a reaction between two solids is being sought.

In another experiment of this type, a 1:1 ratio of CdI_2 and Na_2S was sonicated for a longer period of time at a lower power input. The results obtained are shown in Table 7.3.

TABLE 7.3 Extent of Reaction Between CdI_2 and Na_2S When Sonicated at Low Power.

Time, min	% Conversion	$\left[1-\left(\frac{100-y}{y}\right)^{1/3}\right]^2$
15	5.0	0.000287
30	9.7	0.00112
60	13.6	0.00226
120	20.7	0.00554
180	26.1	0.00920

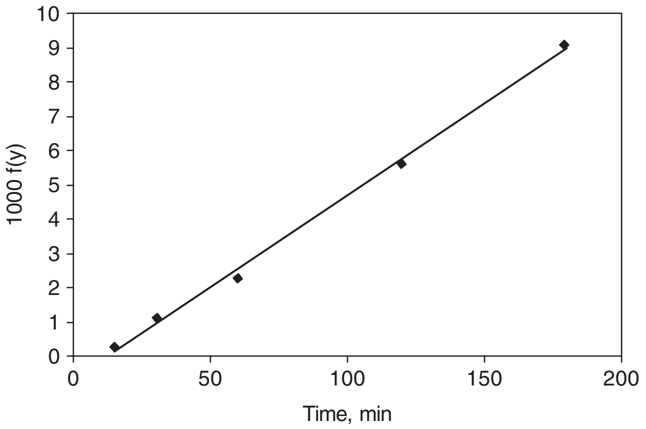


FIGURE 7.7 The results of fitting the Jander equation to data obtained from sonicating a 1:1 mixture of CdI_2 and Na_2S at low power. The function *f*(*y*) is defined in Eq. (7.88).

Fitting the data to the Jander equation gave the results shown in Figure 7.7.

The fit of the data showing the formation of CdS when sonicating a 1:1 mixture of CdI_2 and Na_2S at low power level for an extended period of time to the Jander equation is quite good. The Jander equation has been used as a model for reacting powders for many years, and it works quite well for solids caused to react as a result of the energy supplied by ultrasound. Because of the wide applicability of ultrasound to induce reactions, there is need for a great deal more study along these lines.

This chapter provides an introduction to the principles underlying the reactions of solids. Kinetic studies in this area are not as highly accurate or reproducible as those on reactions in solutions or in the gas phase. However, because of the importance of many solid state reactions, some understanding of how the reactions occur is necessary. Processes such as the drying of solids, crystallization, and decomposition of a wide range of materials make it clear that this area of chemical kinetics will receive more attention in the future.

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PROBLEMS

1. Derive the rate law for the reaction of a gas on the surface of solid particles that are cubic with edge length *l*. Assume that the diffusion of the gas is inversely proportional to the thickness of the product layer. What geometric information does the rate constant contain?

2. Suppose that a gas reacts with solid particles that are thin coin-shaped cylinders, but that the reaction is only on the top and bottom circular faces. Derive the rate law for this reaction assuming that the diffusion of the gas is inversely proportional to the thickness of the product layer. What geometric information does the rate constant contain?

3. In deriving the parabolic rate law, it is assumed that the rate of diffusion of the gaseous reactant is inversely proportional to the thickness of the product layer. Assume that the diffusion of the reactant gas varies as e^{-ax} instead of $1/x$ where a is a constant and x is the thickness of the product layer. Derive the rate law that would result in this case.

4. A solid, A, crystallizes in rods having a rectangular cross section. Suppose that when A is heated, the reaction $A(s) \rightarrow P(g)$ occurs only on the ends of the rods. What would be the rate law for the reaction?

5. A solid compound X is transformed into Y when it is heated at 75°C. A sample of X that is quickly heated to 90°C for a very short time (there is no significant decomposition) and then quenched to room temperature is later found to be converted to Y at a rate that is 2.5 times that when an untreated sample of X when both are heated at 75°C for a long period of time. Explain these observations.

6. Suppose that the reaction $A(s) \rightarrow B(g) + C(s)$ is being studied. Provide a brief discussion of the results and what kind of information the results would provide from studying the effects of each of the following on the rate of the reaction of the $f(\alpha)$ vs. time curve.
   (a) Annealing crystals of A
   (b) Running the reaction under high vacuum
   (c) Prior treatment of A with X-rays
   (d) Varying the particle size of A
   (e) Sintering of A as the reaction takes place

7. For the reaction $A(g) + B(s) \rightarrow C(s)$, the rate is controlled by the diffusion of $A(g)$ through the product layer. Assume that the diffusion is inversely proportional to the thickness of the product layer raised to some power, z. Derive the rate law for this process.

8. For the reaction

$$[Cr(NH_3)_5H_2O]Cl_3(s) \rightarrow [Cr(NH_3)_5Cl]Cl_2(s) + H_2O(g)$$

which was carried out at 85°C, the following data were obtained. It is known that this reaction follows an Avrami type of rate law. Test these data to determine n, the index of reaction.

Time, min	α
0	0
2	0.061
4	0.129
6	0.209
8	0.305
10	0.405
12	0.514
14	0.619
16	0.716
20	0.848
22	0.890
24	0.920
26	0.939
28	0.953

9. When heated at 80°C, the conversion of A into B yields the following data.

t, min	0	10	20	30	40	50
α	0	0.076	0.276	0.538	0.790	0.988

   Assuming that the reaction follows an Avrami rate law, determine the index of the reaction.

10. In many cases, it is found that a solid reacts more rapidly after bombardment with neutrons than it does before. Provide an explanation of this phenomenon.

11. In a rather rare case, the rate of reaction of a solid was found to be slower after it had been subjected to a neutron flux. Provide an explanation of this phenomenon.

12. For many reactions of the type $A(s) \rightarrow B(s) + G(g)$ it is found that the reaction proceeds more rapidly when the average particle is small. Provide a simple explanation of this observation. If the rate is the same (within experimental error) for particles of A having an average

diameter of 10 microns as it is when the average diameter is 30 microns, what does this tell you about the process?

13. The rate of racemization of solid $l - K_3[Co(ox)_3]\bullet 2.6H_2O$ (where ox is oxalate, $C_2O_4{}^{2-}$) is found to increase as the pressure is increased. The value for $\Delta V^{\ddagger}$ from one set of measurements was found to be $-1.44 \pm 0.23\ cm^3/mol$ while a second series of experiments yielded a value of $-1.80 \pm 0.28\ cm^3/mol$. Discuss mechanistic implications that are consistent with the value of $\Delta V^{\ddagger}$. For a discussion of this reaction, see Brady, J., Dachille, F., Schmulbach, C. D. *Inorg. Chem.* **1963**, *2*, 803.

14. The loss of water from the complexes $[Ru(NH_3)_5H_2O]X_3$ (where $X = Cl^-$, Br^-, I^-, or NO_3^-) has activation energies of 95.0, 97.9, 112, and 80.8 kJ/mol, respectively. The values for the entropy of activation are −7.1, −5.2, 5.8, and −15.5 e.u., respectively. In light of the kinetic parameters, discuss the mechanism of dehydration of the complexes.

CHAPTER 8

Nonisothermal Methods in Kinetics

In the last few decades, numerous experimental techniques have been developed that permit the study of several types of changes in a sample as the temperature is increased. Usually the temperature increase is linear, but it is not necessarily restricted to being changed in that manner. As a sample undergoes an increase in temperature, there are several changes that take place. For example, the volume of the sample changes, and this provides the basis for the technique known as *thermal dilatometry*. A structural change other than simple thermal expansion of the solid will usually cause an abrupt change in volume. Also, the reflectance spectrum of the solid will likely show evidence of structural changes. In other cases, complexes such as those of Ni^{2+}, a d^8 ion, may undergo a change from a square planar (D_{4h}) structure to one that is tetrahedral (T_d). This type of isomerization can be studied by several techniques. Because a d^8 ion in a square planar environment has no unpaired electron spins but in a tetrahedral environment they have two unpaired electrons, there is a change in magnetic moment of the sample as it undergoes this type of isomerization. Measuring the magnetic moment of the sample as the temperature is changed allows the progress of the reaction to be followed.

While methods for studying these and other types of changes in the sample have become widely used, the most widely used methods are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As a group, thermal methods of analysis now constitute the most widely used experimental techniques in the chemical industry. A major reason for this widespread use is that determination of bulk properties, thermal stability, and characterization of materials are as important in industrial applications as are the determination of molecular properties.

Moreover, these techniques provide the basis for powerful techniques for studying the kinetics of reactions in solids.

8.1 TGA AND DSC METHODS

While the properties just described are utilized in specific kinds of experiments, the two most common properties studied as temperature is increased are mass and enthalpy. The change in mass as the temperature increases is produced by the loss of volatile products. Therefore, this technique is referred to as *thermogravimetric analysis* (TGA). Although the design of instruments will not be reviewed here, the basic components are a sensitive microbalance and a heat source that surrounds the sample and allows it to be heated at the desired rate.

In *differential scanning calorimetry* (DSC), the heat flow to the sample is compared to the heat flowing to an inert reference as both are heated at the same rate. When an endothermic transition occurs in the sample, the recorder shows a peak, the area of which is proportional to the amount of heat absorbed by the sample. When an exothermic transition occurs in the sample, the opposite effect is seen. Because the difference in electrical power is monitored as the sample and reference have their temperature changed, what is measured is $d\mathrm{H}/d\mathrm{T}$ for the sample. But $d\mathrm{H}/d\mathrm{T} = C_p$, the heat capacity at constant pressure. From thermodynamics, we know that

$$\Delta \mathrm{H} = \int C_p \, \mathrm{dT} \tag{8.1}$$

Therefore, the peak area gives directly the value of ΔH after a calibration of peak area in terms of cal/in^2 or J/in^2 is made using a reaction of known enthalpy. Any type of change in the sample that absorbs or liberates heat can be studied using DSC (fusion, phase transition, decomposition, etc.), while in TGA experiments only those changes that involve a mass loss can normally be studied. In another type of TGA experiment, the sample is suspended in a magnetic field so its mass changes when the magnetic susceptibility of the sample changes (as mentioned earlier for the square planar to tetrahedral isomerization in complexes of d^8 metal ions).

Although several thermoanalytical methods are of potential use in studying reactions occurring in solid state, TGA and DSC are the most often used. Sophisticated equipment, complete with interfaced microcomputer, is available, and these methods are finding wide use in the study of solid

materials. Because both of these methods can readily yield data that are suitable for kinetic analysis, their use for that purpose will be discussed in greater detail. It should be pointed out that this is an area of intense research activity, and the literature in this field has expanded enormously in recent years. The methods that will be described briefly here are included only to show representative examples of the techniques used. Many others have been published and an entire book could easily be written describing nonisothermal kinetics methods and their areas of application. If fact, such sources do already exist (see references at the end of this chapter). In addition, thermoanalytical methods are especially valuable in the polymer industry.

As mentioned earlier, a TGA experiment determines the mass of the sample, either as temperature is held constant or as it is changed in some programmed way. The mass is measured using a microbalance, which is capable of determining a mass loss of 10^{-6} grams. Only a few milligrams of sample are necessary to perform the TGA analysis. TGA is a most useful technique when a reaction of the type

$$A(s) \longrightarrow B(s) + C(g) \tag{8.2}$$

is being studied. In this kind of process, which is characteristic of numerous solid state reactions, the extent of mass loss can be used to establish the stoichiometry of the reaction. Consider a complex represented as $[M(NH_3)_6]X_2$ where M is a metal ion and X is an anion such as Cl^-. Heating a complex of this type in a TGA apparatus *could* produce a curve such as that shown in Figure 8.1.

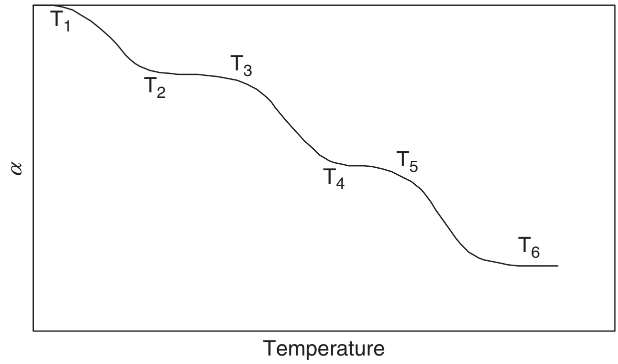

FIGURE 8.1 A hypothetical TGA curve for the loss of six ammonia molecules in three steps as illustrated by Eqs. (8.3) through (8.5).

When complexes such as $[M(NH_3)_6]X_2$ are heated, there is usually a stepwise loss of the volatile ligands, NH_3. The three mass plateaus shown in Figure 8.1 are indicative of the reactions. With the initial and final temperatures being indicated, these reactions could be

$$[M(NH_3)_6]X_2(s) \xrightarrow{T_1 \rightarrow T_2} M(NH_3)_4X_2(s) + 2NH_3(g) \tag{8.3}$$

$$M(NH_3)_4X_2(s) \xrightarrow{T_3 \rightarrow T_4} M(NH_3)_2X_2(s) + 2NH_3(g) \tag{8.4}$$

$$M(NH_3)_2X_2(s) \xrightarrow{T_5 \rightarrow T_6} MX_2(s) + 2NH_3(g) \tag{8.5}$$

Whether these are, in fact, the actual reactions must be determined by comparing the observed mass losses with those expected for the reactions.

Frequently, it is not easy to determine the temperatures $T_1, T_2, \ldots$, owing to the nearly horizontal nature of the curve in those regions and the attendant indistinct beginning and ending temperatures of the reaction steps. This means also that it is not easy to determine accurately the mass loss in such cases. Because of this, some instruments also compute the trace of the first derivative of the mass curve simultaneously. This DTG (derivative thermogravimetric analysis) makes it much easier to determine where a zero slope indicates that the sample is undergoing no change in mass. Therefore, the reaction stoichiometry can be more accurately determined.

Both DSC and TGA allow the fraction of the reaction complete, α, to be determined as a function of temperature. When the mass loss for the reaction being studied has been determined from the plateaus of the TGA trace, the mass loss at specific temperatures can be determined by comparing the mass lost from the beginning of the reaction up to that temperature with the mass loss for the complete reaction. If the mass loss at temperature T_i is W_i and the mass loss for the complete reaction is W_t, then $\alpha = W_i . W_t$. Thus, if a certain reaction corresponds to a mass loss of 40% and the observed mass loss at some temperature is 10%, the value of α at that temperature is $10/40 = 0.25$.

In DSC, the extent of reaction is obtained by first determining the total area of the peak that corresponds to the complete reaction. The required information from the experiment is the fraction of the complete reaction at a series of temperatures so that nonisothermal kinetics procedures can be applied. At a specific temperature, the partial peak area is determined, and the fraction of the complete reaction at that temperature is determined by dividing the area of the peak up to that temperature by the total peak area. A typical endothermic peak in a DSC trace is shown in Figure 8.2. In this case, the temperatures at which α is to be determined are indicated as

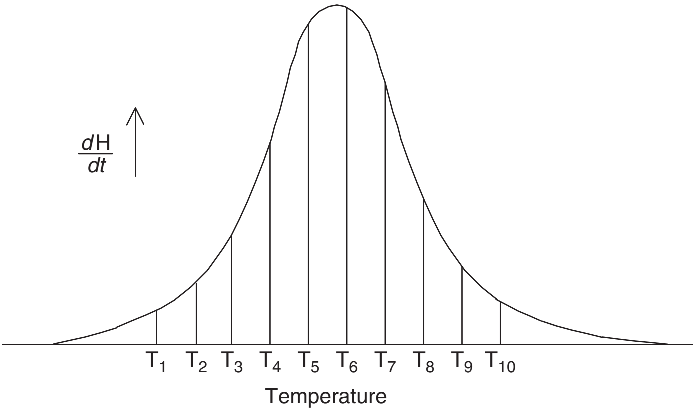

FIGURE 8.2 An illustration showing how to determine α at several temperatures from a DSC trace using partial areas.

$T_1, T_2, \ldots$. For example, the value of α at T_4 is the sum of the partial areas up to that temperature divided by the area of the entire peak. The total peak area is usually available instantly because the computer performs the integration. Partial peak areas are also computed by the instrument simply by entering the temperature up to which the area is needed. Some instruments also come with the software installed to fit the data to various kinetic models, which makes obtaining kinetic data for the process a simple matter. The tedious work of determining areas by graphical means is no longer necessary given the instruments available at this time.

8.2 KINETIC ANALYSIS BY THE COATS AND REDFERN METHOD

While determining reaction stoichiometry is an important use of TGA, our purpose here is to investigate its use in studying reaction kinetics. This is done by employing a rate law that is usually written in the form

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{8.6}$$

where α is the fraction of the reaction complete, t is the time, n is the reaction "order" (more properly, an "index of reaction"), and k is a reaction rate constant. As we saw in Chapter 7, a rate constant for a reaction in the solid state cannot always be interpreted unambiguously.

The rate constant for most chemical reactions can be represented by the Arrhenius equation,

$$k = Ae^{-E_a/RT} \tag{8.7}$$

where E_a is the activation energy, A is the frequency factor (assumed to be independent of temperature, which as shown in Chapter 2 is not always the case), and R is the molar gas constant. As was discussed in Chapter 7, it is necessary to describe the extent of reaction, α, by some rate law. However, in nonisothermal studies, the temperature is changing as well as the time. The connection between the two is provided by the heating rate, which is usually represented by β. If the heating rate is constant (in degrees/minute), β is the change in temperature with time, dT/dt (where T is in K).

After substituting for dt and k in the rate law shown in Eq. (8.6), rearrangement leads to

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} e^{-E_a/RT} dt \tag{8.8}$$

Written in integral form, we have

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^{T} e^{-E_a/RT} dt \tag{8.9}$$

The right-hand side of this equation cannot be integrated directly to provide an analytical expression because it has no exact equivalent. Many of the kinetic methods based on nonisothermal measurements represent different ways of approximating the temperature integral,

$$I = \int_0^{T} e^{-E_a/RT} dt \tag{8.10}$$

The left-hand side of Eq. (8.9) can be integrated for various values of n to obtain several rate laws.

One of the most common ways of circumventing the problem of the temperature integral is to approximate it as a series and then truncate it after a small number of terms. When this is done, the result when $n \neq 1$ is expressed in logarithmic form as

$$\ln \frac{1-(1-\alpha)^{1-n}}{(1-n)T^2} = \ln \frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT} \tag{8.11}$$

In the case where $n = 1$, the equation becomes

$$\ln \ln \frac{1}{1-\alpha} - 2\ln \mathrm{T} = \ln \frac{A\mathrm{R}}{\beta E_a}\left(1 - \frac{2\mathrm{RT}}{E_a}\right) - \frac{E_a}{\mathrm{RT}} \tag{8.12}$$

At room temperature, 2RT is approximately 5 kJ/mol (1.2 kcal/mol), so for most reactions $E_a >> \mathrm{RT}$. As a result, the second term inside the parentheses is negligible, so the term

$$\ln \frac{A\mathrm{R}}{\beta E_a}\left(1 - \frac{2\mathrm{RT}}{E_a}\right) \tag{8.13}$$

can normally be considered to be a constant when fitting data to rate laws. Therefore, the rate equations shown in Eqs. (8.11) and (8.12) can be put in a linear form when the left-hand side is plotted against 1/T. The intercept is $\ln[(A\mathrm{R}/\beta E_a)(1 - (2\mathrm{RT}/E_a))]$ and the slope is $-E_a/\mathrm{R}$. The frequency factor, A, can be calculated from the intercept. It has been stated that only n values of 1, 1/3, 2/3, 1, and 2 have any chemical basis, and examination of the rate laws shown in Table 7.2 indicates that this is the case. Some workers also include the value of 1/2 in the list of possible values.

The way in which the analysis is performed is to determine a series of values for the fraction of the reaction complete, α_i, at a series of temperatures, T_i. Then the functions represented by the left-hand side of the equation are computed for each pair of (α,T) values for various values of n. The values for the functions are then plotted against 1/T, and the series that gives the most nearly linear plot is presumed to correspond to the "correct" reaction index, n. Table 8.1 shows values of α_i and T_i for a hypothetical reaction. Equations (8.11) and (8.12) were used to calculate the $f(\alpha,\mathrm{T})$ values to make plots of these values versus 1/T for the different trial values of n. In keeping with the usual practice, n values of 0, 1/3, 2/3, 1, and

TABLE 8.1 Values of α and $f(\alpha)$ for Various Trial Values of n. When E_a=100 kJ/mol.

T (K)	10^3/T	α	n=0	n=1/2	n=2/3	n=1	n=2
410	2.439	0.06974	−14.695	−14.683	−14.671	−14.659	−14.623
420	2.381	0.14317	−14.024	−13.999	−13.974	−13.948	−13.870
430	2.326	0.27660	−13.413	−13.361	−13.309	−13.255	−13.089
440	2.273	0.49189	−12.883	−12.781	−12.674	−12.564	−12.206
450	2.222	0.77010	−12.480	−12.283	−12.068	−11.833	−11.010
460	2.174	0.97868	−12.284	−11.937	−11.489	−11.195	−8.436

2 were chosen, and the values calculated for the functions when these values were used are also shown in Table 8.1. In this example, the best fit is provided when $n = 2/3$, so the index of reaction is 2/3, but this should not be interpreted too literally as "2/3-order."

Figure 8.3 shows plots of the values of the functions versus 1/T. As can be seen from the figure, the line corresponding to $n = 2/3$ provides the best fit to the data. Of course, that is the value used to generate the α values at different temperatures, so it should provide the best fit.

While this procedure may certainly give an "optimum" value of n with respect to the linearity of the $f(\alpha,T)$ versus 1/T plot, the "order" determined may have no relationship to the molecularity of a transition state in the usual kinetic sense. The n value is usually called the index of reaction. In most cases, the results obtained from this type of analysis are similar to the kinetic parameter determined by conventional isothermal means, and in many cases the agreement is excellent. However, it must be remembered that the original rate law is assumed to have the form

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{8.14}$$

as shown in Eq. (8.6). However, in Chapter 7, it was shown that there are approximately 20 rate laws known to apply to reactions in solids (see Table 7.2). Therefore, it may be that a good fit to the data can be obtained for some value of n applied by means of Eq. (8.11) or (8.12), although the rate law may actually have some other form. A good fit of data as reflected by a high value for a correlation coefficient does not always confirm that a rate law is correct. We will have more to say about this situation later.

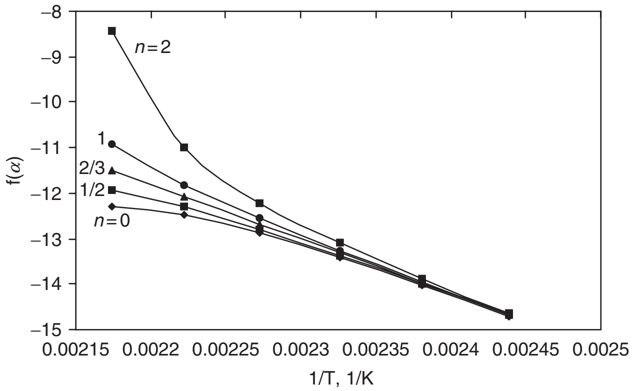

FIGURE 8.3 Coats and Redfern analysis of a reaction for which $n = 2/3$ (see Table 8.1).

The nonisothermal kinetic method described earlier is known as the Coats and Redfern method (Coats and Redfern, 1964). It is only one of many analysis methods that have been developed to analyze data from nonisothermal kinetic studies. It is one of the most widely applied methods, and it is one of the most straightforward procedures. The entire analysis can be programmed for use on a microcomputer or programmable calculator. In this case, the (α,T) data are entered only once, and the entire sequence of n values is tested automatically. The value of n giving the best fit is identified by the correlation coefficient by means of linear regression. Theoretical values of n are 0, 1/3, 1/2 , 2/3, 1, and 2 because they have some justification on the basis of geometrical, contracting, or reaction order models (see Chapter 7). Also, it is possible to treat n as simply an exponent to be varied, and iterative procedures have been devised to identify any value of n that provides the best fit to the data. It is by no means clear what an n value of 0.43 or 1.12 means in terms of a mechanism, however. Although we have arrived at a procedure to identify a value of n, there is no realistic way to relate that value to a mechanism.

8.3 THE REICH AND STIVALA METHOD

An interesting variation on the Coats and Redfern method has been developed by Reich and Stivala (1980). The method makes use of an iterative technique to arrive at the best value of n to fit the α,T data to a rate law. It is best employed using a computer to perform all of the computations. The integrated rate equation is written in the form

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)} = \ln\frac{ART^2}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)e^{-E_a/RT} \tag{8.15}$$

where the temperature integral has been written as a truncated series as before. As before, we recognize that $E_a >> RT$ so that $[1 - (2RT/E_a)]$ is very nearly a constant. Therefore, Eq. (8.15) can be written in a two-point form as

$$\ln\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right] = -\frac{E_a}{R}\left(\frac{1}{T_i}-\frac{1}{T_{i+1}}\right) \tag{8.16}$$

This equation has a linear form when we let y represent the $f(\alpha,T)$ on the left-hand side and x represent $[(1/T_i) - (1/T_{i+1})]$ on the right-hand side.

The slope will be $-E_a/R$, and the intercept will be zero. However, this condition will be met only when the correct value of n is used. For N pairs of (α,T) data, there will be ($N-1$) values of x and y to compute because of the way in which ratios are constructed. Linear regression is performed on these (x,y) data pairs for an initial trial value of n. The form of the equation is such that the intercept will be zero for the correct value of n, but it has a positive and decreasing value as n approaches the correct value. An initial value of $n = 0.1$ is chosen, and the computations are performed with the intercept being compared to zero. If the intercept is greater than zero, n is incremented by 0.1, and the process is repeated. When a value of n results in a *negative* value for the intercept, this means that the "correct" value of n is between that value and the previous value. Therefore, n is decremented to its previous value and step refinement is accomplished by making the increment in n equal to 0.01. The iterative procedure is again implemented until the intercept undergoes another sign change, indicating that the "correct" value of n has been exceeded. At this point, the computation is either repeated using a smaller (0.001) increment to n, or the process is terminated. For all real data, there is no need to try to obtain an n value to three decimal places. It is certainly *not* justifiable to try to attach any "order" significance to a value of, say, $n = 0.837$!

8.4 A METHOD BASED ON THREE (α,T) DATA PAIRS

The Coats and Redfern equation (either in original form or as modified by Reich and Stivala) provides the basis for several numerical procedures for determining a value of n. One such method requires only three (α,T) data pairs when starting with an equation in the form derived by Reich and Stivala. An examination of Eq. (8.16) reveals that when calculations are performed using pairs of (α,T) data a constant value for E_a/R will be obtained only if n has the correct value. Any other (incorrect) value for n will result in the calculated values for E_a/R showing a trend.

In order to provide data for testing the method, the rate equation in differential form (Eq. (8.8)) was solved numerically by means of a fourth-order Runge–Kutta method for specific values of n, E_a, and A. In the calculations, it was assumed that $E_a = 100\,\text{kJ/mol}$ and $A/\beta = 3 \times 10^{10}\,\text{min}^{-1}$. The equation was solved with n assumed to have a value of 5/3, and the calculated values for E_a/R are shown in Table 8.2.

TABLE 8.2 Values of (α,T) and E_a/R Computed Using $n = 5/3$, $E_a = 100\,kJ/mol$, and $A/\beta = 3 \times 10^{10}\ min^{-1}$. A fourth-order Runge–Kutta Method was Used to Compute α from the Differential Rate Equation (Eq. (8.8)).

					E_a/R Values			
Point	$T_1(K)$	α_1	$T_2(K)$	α_2	$n=0.4$	$n=1.2$	$n=5/3$	$n=2$
1	400	0.03177	410	0.06740	11,646	11,891	12,036	12,140
2	410	0.06740	420	0.13369	11,210	11,715	12,016	12,233
3	420	0.13369	430	0.24365	10,452	11,419	12,009	12,441
4	430	0.24365	440	0.39894	9,238	10,931	12,003	12,807
5	440	0.39894	450	0.57706	7,559	10,216	12,000	13,378
6	450	0.57706	460	0.73851	5,619	9,311	11,999	14,150
7	460	0.73851	470	0.85531	3,751	8,321	11,997	15,039
8	470	0.85531	480	0.92584	2,220	7,371	11,995	15,916
9	480	0.92594	490	0.96354	1,104	6,539	11,991	16,668
10	490	0.96354	500	0.98235	347	5,857	11,994	17,258

Note: For $E_a = 100\,kJ/mol$ and $R = 8.31443\,J/mol\ K$, the value of E_a/R is 12,027 K^{-1}.

However, values of E_a/R are also shown when n is assumed to have values of 0.4, 1.2, and 2 in order to show that E_a/R is not constant for these values. Keep in mind that the calculated values for α are shown to far greater accuracy than they could be determined experimentally. This is done to show the completeness of the numerical methods employed.

From the data shown in Table 8.2, it is clear that the value of E_a/R is constant only for the correct value of n (in this case, 5/3 or 1.667). It is also clear that for small values of α, the value of E_a/R does not change much regardless of the value chosen for n. The first step in the analysis is to compute an approximate value for E_a/R, and this is performed using two data pairs, (α_1,T_1) and (α_2,T_2), where α_1 and α_2 are small. The E_a/R is nearly constant for any value of n under these conditions. The first value assigned to the index of reaction, n_o, is zero, and a reasonably accurate value of E_a/R results with n_o as long as α_1 and α_2 are small (see rows 1 and 2 of the E_a/R values shown in Table 8.2). For the first two data pairs, the value of E_a/R varies only from 11,646 to 12,140 as n varies from 0.4 to 2.

After getting an approximate first iterate value for E_a/R, two data points, (α_2,T_2) and (α_3,T_3), are considered, where $\alpha_3 >> \alpha_2$. If $\alpha_3 >> \alpha_2$, maximum variation of the function occurs as the value of n is

changed iteratively. Therefore, a recalculation of E_a/R using these data when one α value is large will give a value close to the test E_a/R computed with the first two data points only when n has approximately the correct value. For example, using $\alpha_2 = 0.06740$ and $\alpha_3 = 0.98235$, E_a/R varies from about 347 for $n = 0.4$ to 17,258 for $n = 2$. Clearly, because the correct value of E_a/R is about 12,000, this value will be obtained only when $n = 1.67$, and the calculated E_a/R is very sensitive to the n value. Using the first iterate E_a/R value, the function

$$F_1 = \frac{\exp\left[\frac{E_a}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right)\right]}{\frac{T_3}{T_2}} \tag{8.17}$$

is calculated using T_2 and T_3. Then the function

$$F_2 = \frac{[1 - (1 - \alpha_2)^{1-n}]}{[1 - (1 - \alpha_3)^{1-n}]} \tag{8.18}$$

is computed with $n_o = 0$, and the result is compared to the value of F_1. It is easily shown that if $F_2 > F_1$, then the iterated reaction index, n', is smaller than the "correct" n ($n' < n$ when $F_2 < F_1$). The process continues by incrementing n' by 0.100001 (so that n' is never exactly equal to 1) and repeating the calculations. At the point where $F_1 > F_2$, n' is greater than n by an amount less than 0.1 for the first iterate determined for E_a/R. This fixes an approximate upper limit of n', usually within 0.1 of the "correct" value. At this point, the value of n' calculated from (α_2,T_2) and (α_3,T_3) using the first iterate E_a/R value is reduced by 0.1, and the increment to n' is reduced from 0.1 to 0.01 as a step refinement. The resulting n' is used to recalculate a second iterate E_a/R value using the first two data pairs. This E_a/R value is very nearly the correct one because the value of n' used is correct to within 0.1.

Having a nearly exact second iterate to E_a/R, the function F_1 is calculated using points (α_2,T_2) and (α_3,T_3). Processing continues by computing the function F_2 iterating with $\Delta n = 0.01$. When $F_2 < F_1$ occurs, the computation ends, and n' has been determined with an upper limit of 0.01 of the "correct" value. If desired, the entire process can be repeated to obtain a third iterate to E_a/R using the value of n', which is very close to the correct value, and an increment of $\Delta n = 0.001$. This is never really necessary, however. The three-point method is very compact and requires a minimum of memory in the computing machine. Therefore, it is adaptable to programmable calculators having small capacity. Exhaustive

calculations using simulated errors in the data have shown that this method actually yields values of n and E_a, which are less sensitive to errors in α than are those based on the Coats and Redfern or Reich and Stivala methods.

8.5 A METHOD BASED ON FOUR (α,T) DATA PAIRS

Another method for determining n and E_a/R from (α,T) data makes use of four data pairs. In this method, it is assumed that four values, α_1, α_2, α_3, and α_4, are known at four temperatures, T_1, T_2, T_3, and T_4, respectively. Further, for simplicity, we will assume that $\alpha_1 < \alpha_2 < \alpha_3 < \alpha_4$. The method makes use of the two-point form of the Coats and Redfern equation, written as

$$\frac{\ln\left[\dfrac{1-(1-\alpha_1)^{1-n}]}{[1-(1-\alpha_2)^{1-n}]}\left(\dfrac{T_2}{T_1}\right)^2\right]}{\dfrac{1}{T_2}-\dfrac{1}{T_1}}=\frac{E_a}{R} \tag{8.19}$$

By considering an analogous equation for the points (α_3,T_3) and (α_4,T_4), elimination of E_a/R yields

$$\frac{\ln\left[\dfrac{1-(1-\alpha_3)^{1-n}]}{[1-(1-\alpha_4)^{1-n}]}\left(\dfrac{T_4}{T_3}\right)^2\right]}{\dfrac{1}{T_4}-\dfrac{1}{T_3}}=\frac{\ln\left[\dfrac{1-(1-\alpha_1)^{1-n}]}{[1-(1-\alpha_2)^{1-n}]}\left(\dfrac{T_2}{T_1}\right)^2\right]}{\dfrac{1}{T_2}-\dfrac{1}{T_1}} \tag{8.20}$$

However, the two sides of this equation will be equal only when n has the correct value. Therefore, it is a simple matter to set up a calculation in which the value of n is changed iteratively until the two sides of the equation are equal using the same type of iteration on n described earlier. A graphical method using this approach has also been described in which the left-hand and right-hand sides of the equation are plotted as functions of n. the point of intersection of the two curves yields the correct value of n. The advantages of this method are similar to those described for the three-point method. It is a compact method that can easily be programmed on a calculator or computer. Also, it is more resistant to errors in α than is either the Coats and Redfern or Reich and Stivala methods, which are both based on the same general rate law shown in Eq. (8.6).

8.6 A DIFFERENTIAL METHOD

Some of the early methods that were developed to analyze data to determine kinetic parameters were based on differential methods. This refers to the fact that the methods do not involve attempts to obtain an integrated rate law, but rather a differential form is used directly. Suppose a reaction follows a rate law that can be written as

$$\frac{d\alpha}{dt} = A\mathrm{e}^{-E_\mathrm{a}/\mathrm{RT}}(1-\alpha)^n \tag{8.21}$$

If the reaction is studied nonisothermally and the heating rate, β, is $d\mathrm{T}/dt$, this rate law can be written as

$$\frac{d\alpha}{d\mathrm{T}} = \frac{A}{\beta}\mathrm{e}^{-E_\mathrm{a}/\mathrm{RT}}(1-\alpha)^n \tag{8.22}$$

Taking the logarithm of both sides of this equation yields

$$\ln\frac{d\alpha}{d\mathrm{T}} = \ln\frac{A}{\beta} - \frac{E_\mathrm{a}}{\mathrm{RT}} + n\ln(1-\alpha) \tag{8.23}$$

When written in terms of the derivative of the left-hand side and $1/\mathrm{T}$, Eq. (8.23) can be written as

$$d\ln\frac{d\alpha}{d\mathrm{T}} = 0 - \frac{E_\mathrm{a}}{\mathrm{R}}d\left(\frac{1}{\mathrm{T}}\right) + n\,d\,\ln(1-\alpha) \tag{8.24}$$

This equation can be rearranged to give

$$\frac{d\left(\ln\dfrac{d\alpha}{d\mathrm{T}}\right)}{d\ln(1-\alpha)} = -\frac{E_\mathrm{a}}{\mathrm{R}}\frac{d(\frac{1}{\mathrm{T}})}{d\ln(1-\alpha)} + n \tag{8.25}$$

Analyzing the data by plotting $d\ln(d\alpha/d\mathrm{T})/d\ln(1-\alpha)$ versus $d(1/\mathrm{T})/d\ln(1-\alpha)$ gives a linear relationship having a slope of $-E_\mathrm{a}/\mathrm{R}$ and an intercept of n. This differential method of analyzing data from noisothermal studies has been in use for many years.

8.7 A COMPREHENSIVE NONISOTHERMAL KINETIC METHOD

A very large number of methods have been developed for treating (α,T) data from nonisothermal kinetic studies to yield kinetic information.

Many of these methods are based on the rate law shown in Eq. (8.6), which is not a general rate law because it can not be put in a form to describe diffusion control or Avrami rate laws (see Chapter 7). In 1983, Reich and Stivala removed the constraint imposed by Eq. (8.6) by developing a kinetic analysis procedure that tests most of the common types of rate laws including Avrami, diffusion control, and others not covered by Eq. (8.6). The method is based on a computer program that fits the (α,T) data to the rate laws and computes the standard error of estimate (SEE) for each so that the rate law that provides the best fit to the data can be identified. It is still true that when data from a large number of runs are considered, it is rare that a given rate law fits the data from all the runs. It is still necessary to make a large number of runs and examine the results to determine the rate law that fits the data from most of the runs.

The 1983 method of Reich and Stivala is still one of the most powerful and useful techniques for studying kinetics of solid state reactions using nonisothermal techniques. The article describing the method also has a listing of the computer program for implementing the procedure (Reich and Stivala, 1983). In general, this method gives excellent agreement with the results obtained from other studies where data from nonisothermal experiments are fitted to the rate laws shown in Table 7.2. In addition to the methods discussed here and in Section 8.3, Reich and Stivala have described a rather large number of data analysis procedures for use in analyzing data from nonisothermal analytical techniques.

8.8 THE GENERAL RATE LAW AND A COMPREHENSIVE METHOD

When the rate laws shown in Table 7.2 are examined, it is found that $(1-\alpha)$, $-\ln(1-\alpha)$, and α occur in various combinations to comprise the rate laws. Moreover, in some of the rate laws, these expressions are raised to some power. Therefore, a general rate law that describes almost any reaction taking place in the solid state can be written to include all of these features. That rate law is for a nonisothermal reaction and is written as

$$\frac{d\alpha}{d\mathrm{T}} = \frac{A}{\beta}\alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p}e^{-E_a/\mathrm{RT}} \tag{8.26}$$

where β is the heating rate and the other symbols have their usual meanings. If the natural logarithm is taken of both sides of the equation, the result is

$$\ln\frac{d\alpha}{d\mathrm{T}} = \ln\frac{A}{\beta} + m\ln\alpha + n\ln(1-\alpha) + p[-\ln(1-\alpha)] - \frac{E_a}{\mathrm{RT}} \qquad (8.27)$$

In this equation, m, n, and p as well as E_a and A are unknowns for a particular reaction. This suggests that if α and $d\alpha/d\mathrm{T}$ were known at five temperatures, a system of five equations containing five unknowns could be solved to find m, n, p, A, and E_a. Of course it would be preferable to have an over-determined system by having many α and $(d\alpha/d\mathrm{T})$ data pairs. Then multiple linear regression could be employed to determine the appropriate values for the five unknown quantities. Such a procedure would enable one to identify any of the rate laws shown in Table 7.2 by determining the appropriate exponents, m, n, and p. For example, if m and p are both zero and $n = 2$, a second-order process is indicated. If m and n are both zero and $p = {}^1\!/_2$, an Avarami A2 rate law is indicated. By varying the exponents appropriately, all of the rate laws shown in Table 7.2 can be reduced to special cases of the general rate law shown in Eq. (8.27).

In Chapter 7, it was shown that in the analysis of the (α,T) data to determine the best-fitting rate law that the *same* rate law was not necessarily indicated as fitting *all* runs, and that numerous runs might be required to obtain a consensus. An elaborate computer program has been developed to solve the system of equations using a numerical technique known as Gauss–Jordan condensation with pivotal rotation (Lowery, 1986). To test the procedure, data known to fit specific rate laws were needed. These data were obtained by solving the general rate law shown in Eq. (8.27) numerically using a fourth-order Runge–Kutta technique. In performing the calculations, solutions were carried out with various combinations of exponents, m, n, and p (e.g., $m = 0$, $n = 1/3$, and $p = 0$; $m = 1/3$, $n = 0$, and $p = 0$; $m = 0$, $n = 1/3$, and $p = 1/3$, etc.). This was done so that the (α,T) from a variety of rate laws could be tested. Also, the general analysis procedure was designed so that the test data could be analyzed not only with a procedure that would determine three exponents, but also one that would keep some of the exponents at zero and "force" the fitting of the data to special case rate laws in which only the other exponents would be allowed to vary. For example, if $m = p = 0$ and only n can vary, the data are forced to fit a rate law having the form

$$\frac{d\alpha}{d\mathrm{T}} = \frac{A}{\beta}(1-\alpha)^n e^{-E_a/\mathrm{RT}} \qquad (8.28)$$

If $m = n = 0$ and only p is allowed to vary, the data are forced to fit a rate law having the form

$$\frac{d\alpha}{d\mathrm{T}} = \frac{A}{\beta}[-\ln(1-\alpha)]^p e^{-E_a/\mathrm{RT}} \tag{8.29}$$

which is the form of the Avrami rate laws. Obviously, if the (α,T) data were calculated using $n = 1/3$ and $m = p = 0$, and then the (α,T) data analyzed using a method that forced them to fit a rate law in which only p could vary, some "interesting" results should be obtained. In order to provide a comparison with other methods, the (α,T) data were also analyzed using the Coats and Redfern method (Eq. (8.11)), and the Reich and Stivala method (Eq. (8.15)) which is based on the same rate law as the Coats and Redfern method.

How well the procedure works is illustrated by the following cases. Table 8.3 shows the results obtained by applying the general procedure to (α,T) data, which were derived from a rate law that is of the form involving a single exponent, $m = 0.333$. In calculating the values used in this case, $n = p = 0$ was assumed. The results shown in the table clearly indicate that any time the general procedure allowed for m to be one of the exponents to be determined, the fit was very good. However, if the procedure used was one in which m was omitted from the computation (n, p, or np type of rate law), the fit was quite poor, as expected. Finally, when the computational procedure used a rate law of the mnp type (all

TABLE 8.3 Results Obtained from the Analysis of Data Derived Using an α^m Type of Rate Law with Data for Which $m = 0.333$ and E_a=100 kJ/mol.

Type[a]	Calculated E_a(kJ/mol)	m	n	p	S[b]
m	100.2	0.332	0.000	0,000	0.36×10^{-9}
n	152.9	0.000	−0.003	0.000	0.48×10^{-9}
p	151.7	0.000	0.000	0.008	0.42×10^{-9}
mn	100.1	0.333	0.000	0.000	0.36×10^{-9}
np	136.5	0.000	0.042	0.102	0.24×10^{-9}
mnp	97.9	0.354	−0.003	−0.007	0.24×10^{-9}

[a] The rate law type refers to the exponents treated as variables and allowed to vary in the data analysis procedure to analyze the (α,T) data.

[b] S is the sum of squares of errors from regression fitting of the data to the rate laws.

TABLE 8.4 Results Obtained from the Analysis of Data Derived Using an $(1-\alpha)^n$ Type of Rate Law with Data for Which $n = 0.333$.

Type[a]	Calculated E_a(kJ/mol)	m	n	p	S[b]
m	−237.1	3.186	0.000	0,000	0.26×10^{-2}
n	100.0	0.000	0.333	0.000	0.84×10^{-9}
p	227.5	0.000	0.000	−1.18	0.26×10^{-3}
mn	100.0	0.000	0.333	0.000	0.84×10^{-9}
np	100.0	0.000	0.333	0.000	0.84×10^{-1}
mnp	101.2	−0.005	0.332	−0.006	0.77×10^{-9}

[a] The rate law type refers to the exponents treated as variables and allowed to vary in the data analysis procedure to analyze the (α,T) data.

[b] S is the sum of squares of errors from regression fitting of the data to the rate laws.

TABLE 8.5 Results Obtained from the Analysis of Data Derived Using a $[-\ln(1-\alpha]^p$ Type of Rate Law with Data for Which $p = 0.333$ (Avrami, A3).

Type[a]	Calculated E_a(kJ/mol)	m	n	p	S[b]
m	−187.7	3.219	0.000	0,000	0.11×10^{-3}
n	73.8	0.000	0.121	0.000	0.51×10^{-4}
p	100.0	0.000	0.000	0.333	0.46×10^{-8}
mn	31.1	1.311	0.072	0.000	0.25×10^{-5}
np	99.9	0.000	0.000	0.333	0.44×10^{-8}
mnp	97.9	0.021	0.001	0.328	0.38×10^{-8}

[a] The rate law type refers to the exponents treated as variables and allowed to vary in the data analysis procedure to analyze the (α,T) data.

[b] S is the sum of squares of errors from regression fitting of the data to the rate laws.

three exponents treated as variables to be determined), the fit was acceptable. In the numerical solution of the differential equation to obtain the (α,T) data, $E_a = 100$ kJ/ was used and that value was successfully determined by the computations using any of the rate laws that tested an "*m*-type" rate law. Similar results are shown in Tables 8.4 and 8.5 for rate laws of the "*n*-type" and the "*p*-type." In each case, the general procedure in which *m*, *n*, and *p* were all determined or any abbreviated

procedure that contained the appropriate rate law exponent successfully analyzed the data to reproduce the values of rate E_a, A, and the exponents.

For the same calculated α, T, and $d\alpha/d$T data that gave the results shown in Table 8.3 when analyzed by the comprehensive method, the Coats and Redfern method gave an n value of approximately zero, an activation energy of 152 kJ/mol, and a correlation coefficient of 1.000! The reason for these totally fictitious results is that the rate law

$$\frac{d\alpha}{d\mathrm{T}} = \frac{A}{\beta}(1-\alpha)^n e^{-E_a/\mathrm{RT}} \tag{8.30}$$

cannot be put in a form that represents a rate law based on α^m, the actual rate law to generate the α and $d\alpha/d$T data. However, the data may be fit by the Coats and Redfern equation with some value of n even if the rate law is of the wrong form.

Table 8.4 shows the results obtained when the rate law used to determine the (α,T) data was of the "n-type" and those data were analyzed using the complete procedure and procedures that involve incomplete forms. To obtain α, T, and $d\alpha/d$T data that were analyzed to give the results shown in Table 8.4, the rate law

$$\frac{d\alpha}{d\mathrm{T}} = \frac{A}{\beta}(1-\alpha)^{1/3} e^{-E_a/\mathrm{RT}} \tag{8.31}$$

was solved numerically. This rate law is of exactly the same form as that used in the Coats and Redfern analysis, so that method would be expected to return the input values for n and E_a. The actual results obtained were $n = 0.33$ and $E_a = 99.7$ kJ/. In this case, either the robust calculation to determine m, n, and p or the method of Coats and Redfern will yield equally reliable results.

In Table 8.5, the results obtained using α, T, and $d\alpha/d$T data that fit an Avrami type of rate law are shown. The general method can, of course, be used to fit rate laws containing any combination of m, n, and p exponents. Clearly, any of the procedures testing a rate law containing the exponent p work well. When analysis of the same $d\alpha/d$T data by the method of Coats and Redfern is attempted, the results are $n = 0.125$ and $E_a = 72.9$ kJ/. There is not agreement between these results and the input data used in solving the rate equation numerically, because the Coats and Redfern method is based on an equation that cannot represent a rate law of the A3 Avrami type, which is based on $[-\ln(1-\alpha)]^{1/3}$ as the function of α.

When methods such as the Coats and Redfern method and others that are based on the same type of limited rate law are used to analyze (α,T) data, satisfactory results are obtained *only* if the rate law being followed is one that can be represented by

$$\frac{d\alpha}{d\mathrm{T}} = \frac{A}{\beta}(1-\alpha)^n e^{-E_a/\mathrm{RT}} \tag{8.32}$$

However, if the (α,T) data are obtained for a reaction that follows some other type of rate law (Avrami, diffusion control, etc.), application of the Coats and Redfern and all similar methods of analysis will give erroneous results *even though the correlation coefficient may be 1.000.* In the past, many studies have not taken this into account, and it has been assumed that a good fit by Coats and Redfern plots assures that a correct law has been identified when in fact the actual rate law may be of some other type. While calculated data based on numerous other combinations of exponents were analyzed, the preceding results serve to show the application of the method based on the comprehensive rate law. The results obtained when two of the three exponents were allowed to vary were similar. For example, in one case where the exponents used to determine the α, T, and $d\alpha/d\mathrm{T}$ data were $m = 0.333$, $n = 0.333$, and $p = 0.333$, the robust calculation returned the values 0.334, 0.334, and 0.331, respectively, and the calculated activation energy was 99.6 kJ/mol. Obviously, the complete procedure can determine the exponents in almost any rate law.

This situation does not necessarily mean that all kinetic data that have been obtained by the Coats and Redfern and similar methods are incorrect. For example, the calculated activation energy frequently has about the same value regardless of whether the correct rate law has been identified or not. That happens because the rate of the reaction responds to a change in temperature according to the Arrhenius equation. The rate law used to fit the kinetic data does not alter the influence of temperature. Also, many kinetic studies on reactions in the solid state have dealt with series of reactions using similar compounds. As long as a consistent kinetic analysis procedure is used, the *trends* within the series will usually be valid. Undoubtedly, however, many studies based on incomplete data analysis procedures have yielded incorrect kinetic parameters and certainly have yielded no reliable information on reaction mechanisms.

The results described in this section show that the general method is quite successful at identifying the correct exponents and activation energy

when a rate law that contains the correct exponent(s) is used. There is, however, a serious problem remaining. The amount of mathematical apparatus is such that *very* accurate values of α, T, and $d\alpha/d$T data are needed to get reasonably accurate values of the exponents m, n, and p. Without the experimental input data being sufficiently accurate, it is still not possible to apply the complete method to uniquely identify the rate law and to determine three exponents. There are sufficient experimental errors and sample-to-sample variations that it is still not possible to identify uniquely a rate law using experimental data using data from most reactions and available instruments. The computer procedure can determine a set of exponents that provide a reasonably good fit to the data, but these constants will likely have enough uncertainty that the rate law will still not be known. Although no evidence will be presented here, the calculations seem to be most sensitive to the values of $d\alpha/d$T that are used in the input data. The experimental techniques used to generate data for studies of this type are TGA and DSC, and advances in instrumentation have been enormous. However, the problems have not been entirely eliminated. Clearly, while great strides have been made in the treatment of data from nonisothermal experiments and kinetic studies on reactions in the solid state have yielded a great deal of information, this branch of chemical kinetics still needs additional development before it will become an exact science. In spite of the difficulties, the best nonisothermal kinetic studies yield results that are comparable in quality to isothermal kinetic studies on solid state reactions.

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PROBLEMS

1. For a certain reaction, the following data were obtained.

T, K	383	393	403	407	413	417	423
α	0.107	0.208	0.343	0.410	0.535	0.623	0.765

Analyze these data using the Coats and Redfern method to determine n and E.

2. Analyze by the Coats and Redfern method the following data for a solid state reaction to determine n, E, and A.

T, K	390	400	410	420	430	440	450
α	0.014	0.032	0.070	0.145	0.283	0.514	0.824

3. Assuming a rate law of the form $d\alpha/dt = k(1 - \alpha)^n$, obtain the integrated rate laws for the values $n = 0$, 1/2, 1, and 2.

4. Use the four data points given to determine the approximate value of n for the reaction A $\rightarrow$ B. Try a few values of n (0, 2/3, 4/3, and 2 should be adequate) with the appropriate functions and make plots to determine the intersection point.

T, K	390	410	430	450
α	0.0143	0.0702	0.2834	0.0845

Having determined n, describe the type of process that is described by this rate law.

CHAPTER 9

Additional Applications of Kinetics

In the previous chapters of this book, many of the important areas of kinetics have been described. These include reactions involving gases, solutions, and solids as well as enzyme-catalyzed reactions. Although these areas cover much of the field of chemical kinetics, there remain topics related to chemical kinetics that do not necessarily fit with the material included in the previous chapters. Therefore, this chapter will be concerned with applications of the principles of kinetics to selected areas that are important in the broad area of chemical sciences. Although not treated from the standpoint of rates of reactions, orbital symmetry is described briefly because of its mechanistic implications.

9.1 RADIOACTIVE DECAY

The kinetics of processes involving radioactive decay are similar in may respects to the treatment of rates of chemical reactions, but some differences arise in special cases. However, some of these cases are frequently encountered, so a brief description of the rate processes will be presented.

The probability of a nucleus decaying is proportional to the number of nuclei present, and all radioactivity processes follow first-order rate laws. The rates are generally independent of the temperature and the chemical environment that surrounds the nuclei. Because the rate is proportional to the number of nuclei, we can write

$$\text{Disintegration rate} = \lambda N \tag{9.1}$$

where N is the number of nuclei present and λ is the *decay constant* (which is analogous to the rate constant, k, for chemical reactions). When

radioactivity is monitored, it is usually by a counting process that measures the number of particles of a specific type that are emitted from the sample. Because not all particles are captured by the counting device, there will normally be an efficiency factor that must be specified. However, for simplicity, we will assume a counting efficiency of 1 and that the counting efficiency remains constant throughout the study. As a result, the counting rate is proportional to the number of nuclei decaying, the *activity* of the sample. The rate law can be written as

$$-\frac{dN}{dt} = \lambda N \tag{9.2}$$

which can be integrated to give

$$\ln\frac{N_o}{N_t} = \lambda t \tag{9.3}$$

This equation is analogous to that obtained for a first-order reaction (see Chapter 1). A plot of ln (activity) vs. time is linear. When written in exponential form, we obtain

$$N_t = N_o e^{-\lambda t} \tag{9.4}$$

By a procedure similar to that used with a first-order reaction, we obtain the half-life as

$$t_{1/2} = \frac{0.693}{\lambda} \tag{9.5}$$

Special cases such as that arising from a nuclide decaying by more than one process simultaneously are treated exactly as the case for parallel reactions (see Chapter 2). In nuclear chemistry, this situation is referred to as *branching* because the overall process is taking different courses. After any given time, the ratio of the product nuclides is the same as the ratio of the decay constant producing them (see Section 2.3). However, there are some situations that arise when describing the kinetics of radioactivity that deserve special mention.

9.1.1 Independent Isotopes

Suppose one is studying the radioactivity that is emitted from a mixture of two isotopes decaying by the same process. Such a mixture might be ^{24}Na (which has a half-life of 15 hours) and ^{32}P (which has a half-life of 14.3 days), both of which decay by β^- emission. If radioactivity of this mixture

is studied by counting the β^- particles emitted, the total activity is the sum of the activities of the two components. In this case, the half-lives are sufficiently different that the early activity is due almost entirely to the decay of ^{24}Na, but after a long time it will have almost entirely disappeared. Therefore, after a sufficient time, the activity will be due almost entirely to the longer-lived nuclide, which is ^{32}P in this case.

When a graph of the logarithm of the total activity versus time is made, the early portion will be approximately linear, and the slope of the line will be $-\lambda_1$ (the decay constant for the shorter-lived component). After several half-lives of the more rapidly decaying component have elapsed, the slope of the line will be approximately $-\lambda_2$ (the decay constant for the longer-lived component). In order to separate the portions of the graph, it is necessary that the half-lives of the components differ considerably.

If the half-lives of the two components of the mixture are known, the total activity of the sample can be written as the sum of the activities of the two components. These are first-order expressions, so the activity, A, can be expressed as

$$A = A_1^{\mathrm{o}}\,\mathrm{e}^{-\lambda_1 t} + A_2^{\mathrm{o}}\,\mathrm{e}^{-\lambda_2 t} \tag{9.6}$$

Multiplying both sides of this equation by $\exp(\lambda_1 t)$ gives

$$A\,\mathrm{e}^{\lambda_1 t} = A_1^{\mathrm{o}} + A_2^{\mathrm{o}}\,\mathrm{e}^{t(\lambda_1-\lambda_2)} \tag{9.7}$$

The values of λ_1 and λ_2 can be calculated from the known half-lives of the components. If a graph is made of $A\mathrm{e}^{\lambda_1 t}$ versus $\mathrm{e}^{t(\lambda_1-\lambda_2)}$, the result will be a straight line having a slope equal to A_2^{o} and an intercept of A_1^{o}. In this way, the activities of the components of the mixture can be evaluated.

9.1.2 Parent-Daughter Cases

In the type of process described here, a radioactive nuclide decays to produce a daughter, which is also radioactive. In a general way, this is similar to the reaction scheme in which a transient state (intermediate) is produced as $A \rightarrow B \rightarrow C$, but there are also some significant differences depending on the relative half-lives of the parent and daughter. One significant difference between radioactive decay and chemical reactions is that the latter are reversible to some extent, so they tend toward equilibrium. Radioactive decay proceeds to completion. If subscripts 1, 2, and 3 are used to represent the parent, daughter, and final product, respectively, the number of nuclei can be expressed as N_1,N_2, and N_3. The rate constants

for decay of the parent and daughter are λ_1 and λ_2, respectively. For the parent, the decay rate can be expressed as

$$-\frac{dN_1}{dt} = \lambda_1 N_1 \tag{9.8}$$

from which we can write directly

$$N_1 = N_1^{\text{o}}\, e^{-\lambda_1 t} \tag{9.9}$$

In order to express the change in the number of daughter nuclei with time, it is necessary to consider the rate at which the daughter forms and the rate at which it decays. Therefore,

$$\frac{dN_2}{dt} = \text{rate formed} - \text{rate of decay} = \lambda_1 N_1 - \lambda_2 N_2 \tag{9.10}$$

We have already found the expression for the variation of N_1 with time, and by substitution we obtain

$$\frac{dN_2}{dt} = \lambda_1 N_1^{\text{o}}\, e^{-\lambda_1 t} - \lambda_2 N_2 \tag{9.11}$$

This equation can be written in the form

$$\frac{dN_2}{dt} + \lambda_2 N_2 - \lambda_1 N_1^{\text{o}}\, e^{-\lambda_1 t} = 0 \tag{9.12}$$

This is a linear differential equation with constant coefficients that can be solved by conventional techniques. In this case, the coefficients are λ_2 and $\lambda_1 N_1$. This equation has exactly the same form as that which results when describing series reactions, and its solution was presented in Section 2.4. After assuming a solution of the form

$$N_2 = u\, e^{-\lambda_2 t} \tag{9.13}$$

we find that

$$\frac{dN_2}{dt} = -u\lambda_2\, e^{-\lambda_2 t} + e^{-\lambda_2 t}\frac{du}{dt} \tag{9.14}$$

Substituting this value for dN_2/dt in Equation (9.12), simplifying, and solving for du/dt, we obtain

$$\frac{du}{dt} = \lambda_2 N_1^{\text{o}}\, e^{-(\lambda_1 - \lambda_2)t} \tag{9.15}$$

Integration gives

$$u = \frac{\lambda_1}{\lambda_1 - \lambda_2} N_{1o}\, e^{-(\lambda_1 - \lambda_2)t} + C \tag{9.16}$$

where C is a constant. Because we have assumed that the solution has the form shown in Eq. (9.13), we find that

$$N_2 = u^{e^{-\lambda_2 t}} = \frac{\lambda_1 N_1^o}{\lambda_2 - \lambda_1} e^{-\lambda_2 t} + C\, e^{-\lambda_2 t} \tag{9.17}$$

When the amount of daughter initially present is represented as N_2^o, then at $t = 0$

$$N_2^o = \frac{\lambda_1 N_1^o}{\lambda_2 - \lambda_1} + C \tag{9.18}$$

Solving for C and substituting the result into Eq. (9.17) we find after simplifying that

$$N_2 = \frac{\lambda_1 N_1^o}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + N_2^o\, e^{-\lambda_2 t} \tag{9.19}$$

In this equation, the first term on the right-hand side represents the decay of the daughter nuclide that is "born" from the decay of the parent, while the second term describes the decay of any daughter nuclide that is initially present. If no daughter nuclide is initially present, Eq. (9.19) reduces to

$$N_2 = \frac{\lambda_1 N_1^o}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \tag{9.20}$$

In the preceding equations, N_1 and N_2 give the number of nuclei of parent and daughter present as a function of time. However, the *decay rate* is the decay constant multiplied by the *number of nuclei*, so the decay rate of the daughter can be expressed as

$$\lambda_2 N_2 = \frac{\lambda_1 \lambda_2 N_1^o}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + \lambda_2 N_2^o\, e^{-\lambda_2 t} \tag{9.21}$$

When the relative decay rates of the parent and daughter are taken into account, there are special cases that can arise. Three of these cases arise in enough instances to warrant a more complete description of them.

Case I. Transient Equilibrium. When the parent has a half-life that is longer than that of the daughter, $\lambda_2 > \lambda_1$. Therefore, after a sufficiently

long time, $e^{-\lambda_2 t} < e^{-\lambda_1 t}$ and $N_2 e^{-\lambda_2 t}$ becomes negligibly small. The expression giving N_2 as a function of time reduces to

$$N_2 = \frac{\lambda_1 N_1}{\lambda_2 - \lambda_1} e^{-\lambda_1 t} \tag{9.22}$$

However, we know that

$$N_1 = N_1^{o} e^{-\lambda_1 t} \tag{9.23}$$

so taking the ratio N_1/N_2 gives

$$\frac{N_1}{N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_1} = \text{a constant} \tag{9.24}$$

If the counting efficiencies of the parent and daughter are the same, the numbers of nuclei can be replaced by the activities to give

$$\frac{A_1}{A_2} = \frac{\lambda_2 - \lambda_1}{\lambda_1} \tag{9.25}$$

Early in the decay scheme, the total activity passes through a maximum as the long-lived parent decays to produce a daughter that is decaying rapidly. After some period of time (that depends upon the relative magnitudes of λ_1 and λ_2), the total activity begins to decrease at a rate that is approximately constant. This occurs because the parent is decaying at a constant rate, and the daughter is decaying at the same rate because the amount of daughter is determined by the decay rate of the parent. When the logarithm of the activities of the parent and daughter are plotted versus time, the result is as shown in Figure 9.1.

Case II. Secular Equilibrium. In a situation where the parent has a half-life that is much greater than that of the daughter, the activity from the decay of the parent does not decrease to any great extent on a timescale that is several half-lives of the daughter. Therefore, $\lambda_2 >> \lambda_1$. Because the *formation* of the daughter occurs by the decay of the parent, the rate of formation of the daughter can be expressed as

$$\frac{dN_2}{dt} = \lambda_1 N_1 \tag{9.26}$$

The rate of decay of the daughter is given by

$$-\frac{dN_2}{dt} = \lambda_2 N_2 \tag{9.27}$$

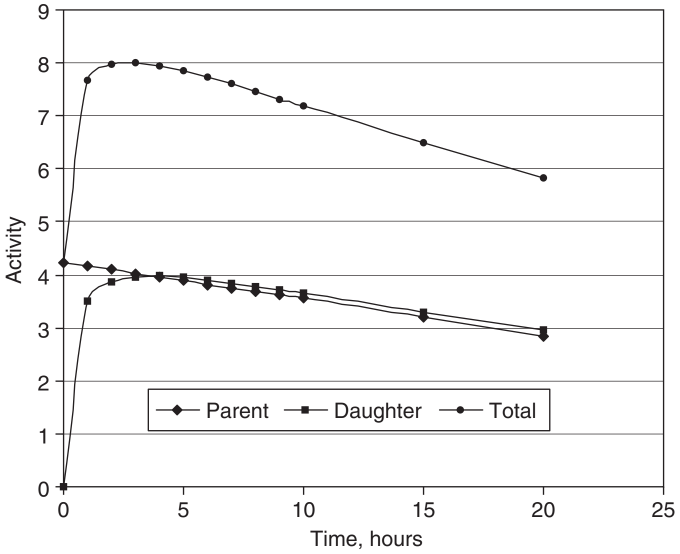


FIGURE 9.1 Activity of parent and daughter and total activity during transient equilibrium. Note how the activity of the daughter becomes virtually equal to that of the parent at longer times. Data are based on a parent having a half-life of 10 hours and a daughter having a half-life of 1.0 hours. Activity is in arbitrary units.

After a sufficiently long time, equilibrium is established in which the rate of formation of the daughter is equal to the rate of its decay. The number of parent nuclei is given by

$$N_1 = N_1^{\mathrm{o}}\, \mathrm{e}^{-\lambda_1 t} \tag{9.28}$$

so the decay rate of the parent is

$$\lambda_1 N_1 = \lambda_1 N_1^{\mathrm{o}}\, \mathrm{e}^{-\lambda_1 t} \tag{9.29}$$

However, this must also be the rate of formation of the daughter. Therefore,

$$\frac{dN_2}{dt} = \lambda_1 N_1^{\mathrm{o}}\, \mathrm{e}^{-\lambda_1 t} \tag{9.30}$$

After a sufficiently long time that "equilibrium" is established, the activity of the daughter is equal to that of the parent. At that time,

$$\lambda_2 N_2 = \lambda_1 N_1\, \mathrm{e}^{-\lambda_1 t} \tag{9.31}$$

When compared to the decay constant of daughter, which is much larger, the decay constant of the parent is negligibly small ($\lambda_1 \approx 0$) and $e^{-\lambda_1 t} \approx 0$. Consequently,

$$\lambda_2 N_2 = \lambda_1 N_1^{\text{o}} \tag{9.32}$$

and since the number of parent nuclei is approximately equal to the number initially present, $N_1 \approx N_1^{\text{o}}$. When $N_2^{\text{o}} = 0$ and the time of decay is much shorter than the half-life of the parent, Eq. (9.21) reduces to

$$\lambda_2 N_2 = \lambda_1 N_1^{\text{o}} \left(1 - \mathrm{e}^{-\lambda_2 t}\right) \tag{9.33}$$

At $t = 0$, $\lambda_2 N_2 = 0$ and the total activity is that of the parent. After a time equal to the half-life of the daughter, the decay constant is $\lambda_2 = 0.693/t_{1/2}$, where $t_{1/2}$ is the half-life of the daughter. Therefore,

$$\left(1 - \mathrm{e}^{(0.693/t_{1/2})(t_{1/2})}\right) = 0.5 \tag{9.34}$$

and $\lambda_2 N_2 = 0.5\lambda_1 N_1$. After a time equal to two half-lives of the daughter has elapsed,

$$\left(1 - \mathrm{e}^{(0.693/t_{1/2})(2t_{1/2})}\right) = 0.75 \tag{9.35}$$

Therefore, the activity of the sample is initially that of the parent, but it increases as more daughter is produced. After a many half-lives of the daughter have elapsed, the activity as $t \to \infty$ is $\lambda_2 N_2 = \lambda_1 N_1$, which shows that the total activity will be twice that of the parent, $2\lambda_1 N_1$. In other words, the activity of the parent has continued essentially constant while the activity of the daughter has increased to a value equal to that of the parent. Figure 9.2 shows the relationship for activity of the sample as a function of time.

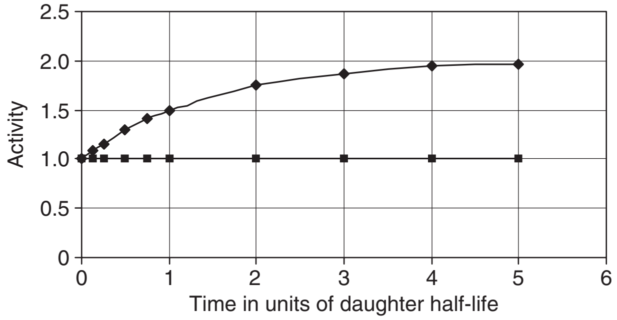
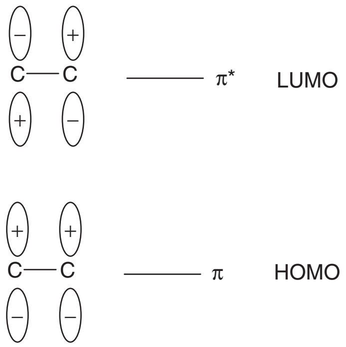


FIGURE 9.2 Activity of a sample exhibiting secular equilibrium. The timescale is in units of half-life of the daughter and activity is in arbitrary units. Note how the total activity approaches a value that is twice that of the parent at longer times.

If the parent has a shorter half-life than the daughter, neither of these ''equilibrium'' conditions is met. The amount of the daughter increases, goes through a maximum, and then decreases. Eventually, the parent will have decayed almost completely, and the activity of the sample will be that of the daughter alone with the activity determined by the half-life of the daughter.

9.2 MECHANISTIC IMPLICATIONS OF ORBITAL SYMMETRY

As a reaction occurs between molecules, electrons are involved as the orbitals on one molecule interact with those on another. In a general way, the electrons in the highest occupied molecular orbital (generally called the HOMO) of a molecule become attracted to or shared with the lowest unoccupied molecular orbital (identified as the LUMO) on the other. These outer orbitals are often referred to as the *frontier orbitals*. As is known from other areas of chemistry, the outer orbitals must have matching symmetry for overlap to be effective. For example, in the ethylene molecule, the two combinations of the p orbitals not used in σ bonding can be shown as



Since the LUMO has the symmetry as just shown, another molecule approaching the ethylene molecule would need to have the same symmetry for a reaction to occur. In that case, the reaction would be considered as *symmetry allowed*. If the symmetry does not match that of the LUMO of ethylene, the reaction would be *symmetry forbidden*. In other words, for overlap to be positive ($S > 0$), the HOMO on one of the reacting molecules must have the same symmetry as the LUMO on the other.

In order for orbitals to combine effectively to form bonding molecular orbitals, the atomic states must have similar energies. Therefore, it is necessary for the difference between the HOMO in one molecule and the LUMO in another to be less than some threshold amount. As the reaction occurs, a bond is broken in one molecule as one forms in another. When both orbitals are of bonding character, the bond being broken (as electron density is being donated to the other molecule) is the one representing the HOMO in one reactant, and the bond being formed is represented by the LUMO in the other (which is empty and receives electron density as the molecules interact). When the frontier orbitals are antibonding in character, the LUMO in one reactant molecule corresponds to the bond being broken and the HOMO to the bond formed.

A consideration of the N_2 and O_2 molecules provides a simple illustration of how these principles apply to reactions. The HOMOs of the N_2 molecule are π_u in symmetry, which are antisymmetric, while the LUMOs of O_2 are half-filled π_g (usually designated as π^* or π_g^*) in symmetry. This can be seen by looking at the molecular orbital diagrams for these molecules shown in Figure 9.3.

Therefore, interaction of the half-filled π_g orbitals of O_2 with the filled π_u orbitals of N_2 is symmetry forbidden. Electron density could flow from the half-filled π_g HOMO of O_2 to the empty π_g orbitals on N_2, but that is contrary to the nature of the atoms based on their electronegativities. Therefore, transfer of electron density from O_2 to N_2 is excluded for chemical reasons. As a result, the reaction

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \tag{9.36}$$

does not take place readily and is accompanied by a high activation energy.

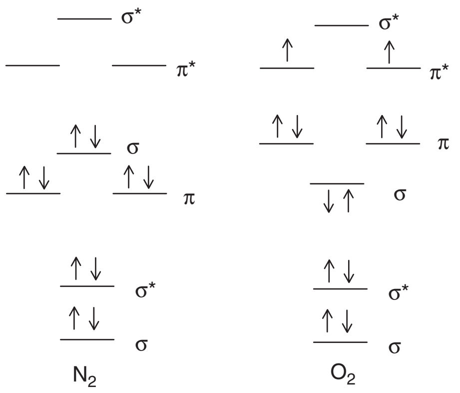
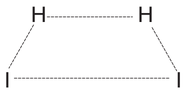


FIGURE 9.3 Molecular orbital diagrams for N_2 and O_2 molecules.

The reaction between H_2 and I_2 was described in Chapter 1. This reaction would be possible as a result of the transfer of electron density from H_2 to I_2 on the basis of their electronegativities. However, the LUMO for I_2 is an antibonding orbital that has σ_u symmetry, while the HOMO for hydrogen is σ_g. Therefore, in the expected interaction,



would result in an overlap of zero for these two orbitals. This can be shown with regard to orbitals as illustrated in Figure 9.4. Consequently, the overlap is zero for the HOMO of the H_2 molecule with the LUMO of an I_2 molecule, and the expected interaction is symmetry forbidden. Although transfer of electron density from filled molecular orbitals on I_2 to an empty σ_u orbital on H_2 is not forbidden by symmetry, it is contrary to the difference in electronegativity. As a result of the symmetry character, the expected bimolecular reaction involving molecules does not occur. In this case, the reaction occurs between a molecule of hydrogen and two iodine atoms, which is not symmetry forbidden.

Another reaction that can be described in terms of orbital symmetry is the ring closing reaction of *cis*–1,3–butadiene to produce cyclobutene. The reaction is an example of a class of reactions known as *electrocyclic* reactions. There are two different pathways that can be imagined for this reaction, which can be illustrated as shown in Figure 9.5. Both mechanisms involve rotation of the terminal CH_2 groups but in different ways.

In the conrotatory mechanism (shown in Figure 9.5a), the two CH_2 groups rotate in the *same* direction. In the disrotatory mechanism (shown in Figure 9.5b), they rotate in *opposite* directions. It is easy to see that the two mechanisms do not lead to a product having the same stereochemistry.

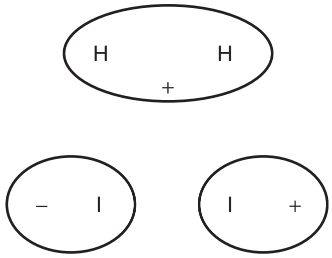


FIGURE 9.4 Symmetry of the HOMOs in H_2 and I_2.

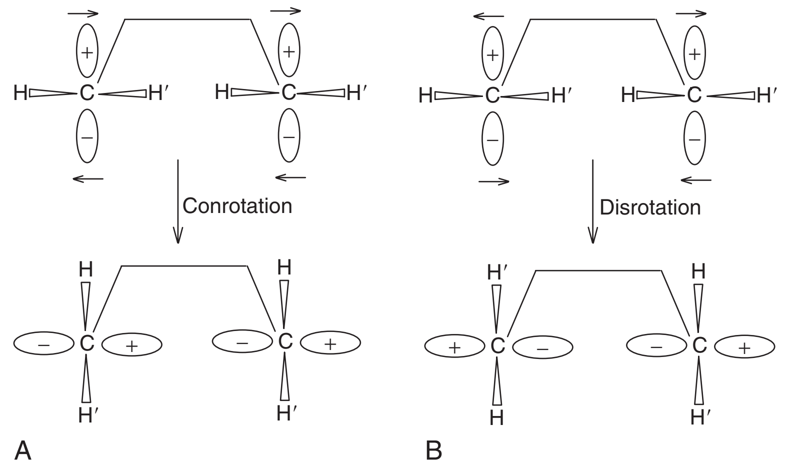


FIGURE 9.5 Conrotation and disrotation of terminal methylene groups in *cis*–1,3–butadiene.

In each case, one hydrogen atom is labeled as H′ to distinguish it from the other. The conrotatory mechanism would lead to both H′ atoms being on the *same* side of the ring, while disrotation would place them on *opposite* sides of the cyclobutadiene ring.

Figure 9.6 shows a simplified structure of 1,3–butadiene with the symmetry of the HOMO indicated on the orbitals. The effect of conrotation (a) and disrotation (b) of the terminal methylene groups is also shown. Note that in this case disrotation of the two methylene groups leads to plus and minus lobes of the orbitals being brought close enough together to interact. That combination leads to zero overlap, which accordingly does not lead to bond formation. On the other hand, conrotation leads to lobes of the same sign being brought together, which does lead to bond formation and which gives ring closure. Experimentally, it is found that when 1,3–butadiene is heated an electrocyclic ring closure takes place in which the H′ atoms are found on opposite sides of the ring in 100% of the product. Although H′ may be a deuterium atom, other substituents may be used. If one hydrogen atom is replaced in each methylene group, they are found on opposite sides of the ring after closure has taken place.

Excitation of 1,3–butadiene photochemically causes excitation of an electron from the HOMO to the LUMO, which has different symmetry. Figure 9.7 shows the LUMO of 1,3–butadiene and how the orbital is affected by both conrotation and disrotation.

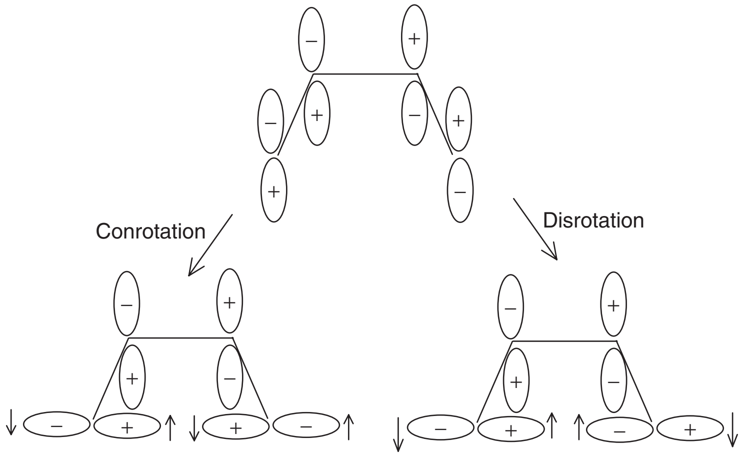


FIGURE 9.6 Symmetry of the HOMO of 1,3–butadiene and the changes that occur during conrotation and disrotation.

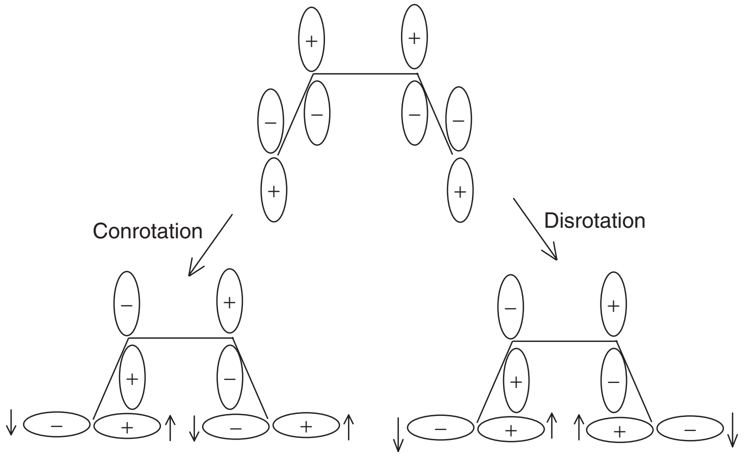


FIGURE 9.7 Symmetry of the LUMO of 1,3–butadiene and the changes that occur during conrotation and disrotation.

Note that for the LUMO the signs of the orbitals are different so that conrotation leads to no net overlap. On the other hand, disrotation brings orbitals together that have the same sign, which leads to favorable overlap. Disrotation places the H′ atoms on the same side of the ring, and this product is found when ring closure is induced photochemically.

Electrocyclic ring closure of *cis*–1,3,5–hexatriene leads to the formation of 1,3–hexadiene. Although the hexatriene molecule is planar, the product

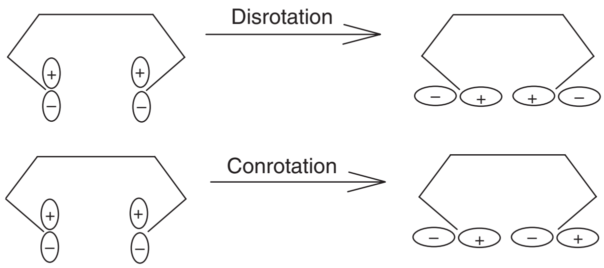


FIGURE 9.8 Disrotation and conrotation in 1,3,5–hexatriene.

of cyclization has two CH_2 groups in which the four hydrogen atoms are located with two above the ring and two below it. Therefore, in the transition state the terminal CH_2 groups can undergo either conrotation or disrotation as shown in Figure 9.8.

The rotation of the terminal CH_2 groups involves breaking a π bond formed from p orbitals on two carbon atoms so they can form a σ bond. In order to obtain positive overlap, the orbitals must match in symmetry, which occurs during a disrotatory pathway. Conrotation of the groups would lead to zero overlap. Therefore, the formation of the σ bond that leads to ring closure must occur as a result of disrotation of the methylene groups.

The guiding principle regarding how electrocyclic reactions occur was provided by R. B. Woodward and R. Hoffmann. The rule is based on the number of electrons in the π bonding system of the molecule. That number of electrons can be expressed as either $4n$ or $4n + 2$, where $n = 0, 1, 2, \ldots$. This rule predicts the mechanism of electrocyclization in terms of conrotation or disrotation as follows.

$4n = 4, 8, 12, \ldots$, thermal cyclization is conrotatory.

$4n + 2 = 2, 6, 10, \ldots$, thermal cyclization is disrotatory.

The rule can be described as if the number of π electrons is expressed as $4n + 2$, the reaction occurs so that the p orbitals involved in thermal closing the ring will result in bond formation when the rotation is disrotatory. The reaction is photochemically allowed when the rotation is conrotatory. When the number of π electrons is expressed as $4n$, thermally induced closure occurs by conrotatory movement but photochemical closure allowed by disrotatory movement.

According to the principle of microscopic reversibility, the lowest energy pathway for the forward reaction is also the lowest energy pathway for

the reverse reaction. Therefore, ring opening reactions are predicable by making use of the same rules that are based on the number of electrons in the π system.

Applying this rule in the case of 1,3–butadiene, which has four electrons in the π system, predicts that cyclization would occur as a result of conrotation as was deduced earlier. The cyclization of 1,3,5–hexatriene (which has six π electrons) occurs by disrotation. It must be remembered that these predictions apply to *thermally* induced cyclizations and that photochemical excitation produces an excited state that causes the rules stated previously to be reversed for that type of reaction.

The preceding discussion illustrates how the study of reaction mechanisms is augmented by an understanding of simple aspects of molecular orbital theory. We have described only a very limited number of reactions, and there are many others for which the mechanisms can be predicted on the basis of orbital symmetry. For more details on this important subject, consult the references listed at the end of this chapter.

9.3 A FURTHER LOOK AT SOLVENT PROPERTIES AND RATES

In Chapter 5, many facets of kinetic studies on reactions carried out in solutions were discussed. However, we did not describe at that time the many correlation schemes that have been developed to correlate reaction rates with properties of the solvents. Therefore, that important and useful topic will be described briefly in more detail here. To have also included in Chapter 5 the material presented in this section would have lengthened that chapter too greatly. It should be remembered that entire books have been written on the effects of solvents, so even with the discussion presented in this section the coverage is far from complete.

Because an enormous number of reactions are carried out in solution, the choice of a solvent becomes a crucial consideration with regard to reaction times as well as the course of the reactions in general. In view of the importance of this issue, it is not surprising that a large body of literature has developed regarding solvent influences. Although in Chapter 5 the solubility parameter was shown to have broad applicability, it is by no means the only parameter devised to correlate rates with solvent properties (Reichardt, 2003; Drago, 1992; Lowry and Richardson, 1987; Schmid and Sapunov, 1982). In fact, there are approximately two dozen "polarity

scales'' that have been devised, but only a few of the more common ones will be described. Some are based on dipole moment, dielectric constant, or other properties of the solvent molecules. In view of this vast body of literature and the importance of the topic, it is appropriate to describe briefly a few of the approaches that have been taken.

From the outset, it should be recognized that a solvent produces effects on both the activation energy and the activation entropy. The equilibrium that leads to the formation of the transition state is governed by the relationship

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\,\Delta S^{\ddagger} = -RT\ln K^{\ddagger} \tag{9.37}$$

with the rate constant being determined by the concentration of the transition state, which is determined by the magnitude of $K^{\ddagger}$. Figure 9.9 shows a general indication of the effect produced by two solvents, S1 and S2, on the activation energy.

The effect of the solvent on the rate of a reaction is the result of lowering the free energy of formation of the transition state by changing the enthalpy, entropy, or both. This could also result from changing the state of the reactants, because it is the difference between the free energies of the reactants and the transition state that determines $\Delta G^{\ddagger}$. For this discussion,

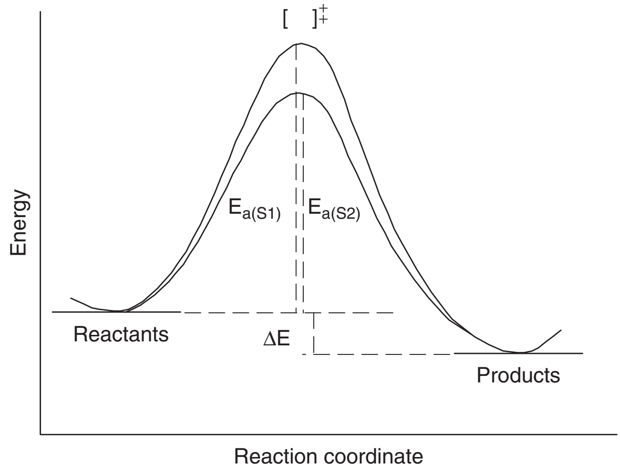


FIGURE 9.9 Profiles for a reaction carried out in two solvents. The activation energies for the reaction in the two solvents are $E_{a(S1)}$ and $E_{a(S2)}$, with solvent 2 being one that enhances the formation of the transition state.

we will assume that the effect on the rate is the result of changes in the transition state.

If we suppose that in one solvent the equilibrium constant for the formation of the transition state has a value of 1.00, then $-\Delta G^{\ddagger}/RT = \ln K^{\ddagger} = 0$ and $\Delta G^{\ddagger} = 0$. In order to change the equilibrium constant to 2.00 (which would double the rate), then $-\Delta G^{\ddagger}/RT = 0.693$ so that $-\Delta G^{\ddagger} = 0.693 \times RT$, which at 25°C means that $-\Delta G^{\ddagger} = 1.72$ kJ/mol. This effect could be caused (if there is no change in $\Delta S^{\ddagger}$ between the two solvents) by a change in $\Delta H^{\ddagger}$ of only the same amount. Even changing the rate by a factor of 10 (by changing $K^{\ddagger}$ by that factor) would require a change in $-\Delta G^{\ddagger}/RT = 2.3$ or a change in $-\Delta G^{\ddagger}$ of 5.7 kJ/mole (or by the same change in $\Delta H^{\ddagger}$ if $\Delta S^{\ddagger} = 0$). Similarly, if $\Delta H^{\ddagger} = 0$, a change in $T\Delta S^{\ddagger}$ can produce a factor of 2 change in $K^{\ddagger}$ with a change of only 5.8 J/mol K in $\Delta S^{\ddagger}$. Even to produce a 10-fold increase in rate would require only a 19 J/mol K change in $\Delta S^{\ddagger}$. Clearly these modest changes in thermodynamic properties are within the realm of differences in solvation effects on the transition state.

The interaction that occurs between the solvent and the transition state is sometimes described in terms of specific and nonspecific, depending on the nature of the interaction. *Specific* interaction refers to hydrogen bonding or charge transfer complexation. *Nonspecific* interaction is the result of general attraction due to van der Waals forces. Some of the correlations that have been devised are restricted to only nonspecific solvation of the transition state by the solvent.

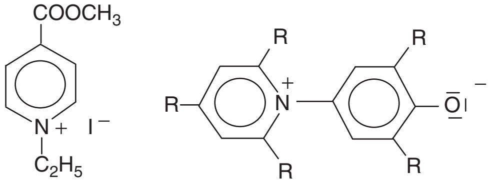
It might be expected that rates of reactions would vary in a systematic way with dipole moment of the solvent. That this is *not* likely can be seen by considering the solvents water and nitrobenzene. Water has a dipole moment of 1.85 D while that of $C_6H_5NO_2$ is 4.22 D. However, because the charge separated in nitrobenzene is spread out over a large molecule, there is no small, localized region of charge to strongly solvate a transition state that has a charge separation. Also, the size of the nitrobenzene molecule prevents it from effectively surrounding a smaller species. The result is that water (or other solvents consisting of small molecules such as CH_3OH, CH_3NO_2, or CH_3CN, all of which have smaller dipole moments) enhances the rates of reactions in which the transition state has charge separated to a greater extent than does nitrobenzene.

Because the ability of a solvent to solvate ions is dependent on the dielectric constant, it is natural to attempt to correlate rates of reactions that involve charged species with this parameter. Dielectric constants (ε)

vary from slightly over 2 for liquids such as carbon tetrachloride and benzene, to 78.4 for water, to over 100 for formamide and methyl formamide. For reasons that will not be explained fully here, correlations of rate constants with ε usually involve examining the relationship between ln *k* and ln ε. For certain reactions in a particular series of solvents, good correlations are obtained, but in general rates do not correlate well with ε.

When a solvent molecule becomes attached to a solute (which may be a reactant or a transition state), the electrons in frontier orbitals are affected to some extent. Therefore, when the solvated species undergoes an electron transition, absorption occurs at wavelengths that vary somewhat with the nature of the solvent. It is possible to make use of the spectral shifts (the so-called *solvatochromic effect*) to give some indication of the strength of solvent-solute interactions.

When certain molecules (sometimes referred to as *probes*) are surrounded by solvent molecules, charge transfer complexes form. Studying the charge transfer absorption bands (usually in the UV) as the solvent is varied yields spectra that show maxima in different positions depending on the ability of the solvent to attach to the solute. As a result, a scale based on the positions of the maxima of bands in the spectrum can be devised to describe "solvent polarity." Several such scales exist, which generally depend on the nature of the probe molecules. Two such probes that have been used are the following.



I II

Because the electron transitions involve moving an electron to an antibonding (π^*) orbital, the polarity scale is sometimes called a π^* scale. Many variations of this type have been described, and of course the actual numerical values are different but generally show similar *trends* for a series of solvents.

A solvent scale that is also based on electronic transitions in structure II (shown earlier) in several solvents was developed by Reichardt. The parameters, known as the E_T scale, have been widely used to correlate rate constants for reactions carried out in various solvents. Table 9.1 shows some representative values for E_T, which generally fall in the range 30–70.

TABLE 9.1 Values for E_T, SPP, and Solubility Parameters (δ) for Selected Solvents.

No.	Solvent	E_T[a]	δ, h	SPP[b]	π^{*c}
1	*n*–Hexane	30.9	7.3	0.591	−0.11
2	Diethyl ether	34.6	7.66	0.694	0.24
3	Cyclohexane	31.2	8.20	0.557	
4	Carbon tetrachloride	32.5	8.7	0.632	0.21
5	Mesitylene	32.9	8.81	0.576	0.45
6	Benzene	34.5	9.06	0.667	0.55
7	Tetrahydrofuran	37.4	9.50	0.838	0.55
8	Cyclohexanone	39.8	9.57	0.874	0.71
9	Acetone	42.2	9.76	0.881	0.62
10	1,4–Dioxane	36.0	10.0	0.701	0.49
11	Acetic acid	51.9	10.45		
12	Pyridine	40.2	10.6	0.922	0.87
13	Dimethylformamide	43.8	12.14	0.954	0.88
14	Nitromethane	46.3	12.25		
15	Ethanol	51.9	12.96	0.853	0.85
16	Dimethylsulfoxide	45.0	13.0	1.000	1.00
17	Acetonitrile	45.6	13.0	0.895	0.66
18	Methanol	55.5	14.48	0.857	0.86
19	Water	63.1	23.4		
20	*n*–Pentane		7.1	0.507	−0.15
21	*n*–Heptane		7.5	0.526	−0.06
22	Methylcyclohexane		7.8	0.563	
23	*n*–Dodecane		7.8	0.571	−0.01
24	*o*–Xylene		8.84	0.641	
25	Toluene		8.9	0.655	0.49
26	Methyl acetate		9.15	0.785	0.49
27	Chloroform		9.3	0.786	0.69
28	Methyl formate		9.56	0.804	0.55
29	Anisole		9.52	0.823	0.70
30	Chlorobenzene		9.59	0.824	0.68
31	Bromobenzene		10.5	0.824	0.84
32	Tetrahydrofuran		9.50	0.838	0.55
33	1,1,1–Trichloroethane		8.62	0.850	0.44
34	Dichloromethane		9.89	0.876	0.73
35	Butyronitile		9.99	0.915	0.63
36	Benzonitrile		9.70	0.960	0.88
37	Nitrobenzene		11.6	1.009	0.86

[a]From Lowry and Richardson, 1987; [b]from Catalán, 1995; [c]from Laurence, et al., 1994.

Catalán (1995) has developed a set of polarity parameters known as the solvent bipolarity-polarizability (SPP) scale. Like the π^* scales, the SPP parameters are based on the ability of the solvent to shift the positions of absorption bands in a test molecule used as a probe. The effect, known as *solvatochromism*, utilizes 2–(*N*,*N*–dimethylamino)–7–nitrofluorene (DMANF) by measuring the shift in the absorption spectrum as a series of solvents is used. The value of SPP for each solvent is calculated from the relationship

$$\mathrm{SPP} = \frac{\Delta\bar{\nu}_{(\mathrm{solvent})} - \Delta\bar{\nu}_{(\mathrm{gas})}}{\Delta\bar{\nu}_{(\mathrm{DMSO})} - \Delta\bar{\nu}_{(\mathrm{gas})}} \tag{9.38}$$

On this scale, solvents generally have values ranging from about 0.4 to 1.0, although a few lie outside this range. Values for the SPP parameter for numerous solvents are shown in Table 9.1.

So much has been made about correlations of rate constants with various solvent parameters that it is tempting to look for correlations among the parameters themselves. Table 9.1 includes both the E_T values and solubility parameters for 19 common solvents, so a relationship was established between the δ and E_T values for those solvents. From the data presented, it is easily seen that as the solubility parameter increases so does the value of E_T. However, in order to clarify the relationship, Figure 9.10 was prepared.

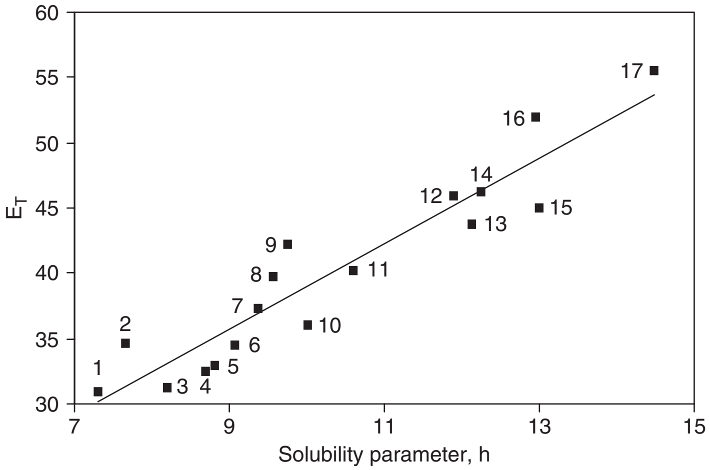


FIGURE 9.10 The relationship between solvent E_T values and solubility parameters. The numbers correspond to those for the solvents as listed in Table 9.1. Although included in the table, the points for acetic acid and water are not shown.

It can be seen that while the correlation is not outstanding, there is a general relationship between the π^* value and the solubility parameter.

Although it is not particularly surprising, the relationship between the E_T values for solvents and their solubility parameters is linear, and the correlation coefficient is 0.945. Both parameters are related to intermolecular forces that exist between the molecules and those that arise as the solvents interact with the transition state during a reaction. If forming the transition state involves an increase in polarity or generation of charges, the higher the E_T value or the solubility parameter the greater the effect on the rate, so the two sets of parameters should correlate to some extent. However, it is reassuring that the effects correlate so well because both are useful indices of solvent effects on reaction rates. It may be that it does not matter as much *which* set of parameters is used to correlate rates with solvent properties as it does to know what the *trends* indicate about the nature of the transition state.

The previous discussion has alluded to the fact that the various parameters used to describe the effects of solvent are interrelated, and it is interesting to see how the π^* parameter correlates with the solubility parameter. Figure 9.11 shows the relationship for several solvents.

Finally, the relationship between the π^* and E_T values for various solvents is illustrated in Figure 9.12.

Although other solvents fit the relationship rather well, it is obvious that the points for methanol and ethanol fall far from the general trend. These solvents generally do not give typical solvent effects on rates of many

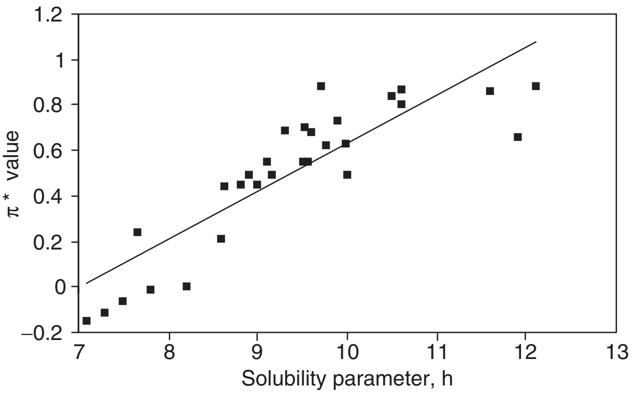


FIGURE 9.11 The correlation between solubility parameter and the π^* value for several solvents shown in Table 9.1.

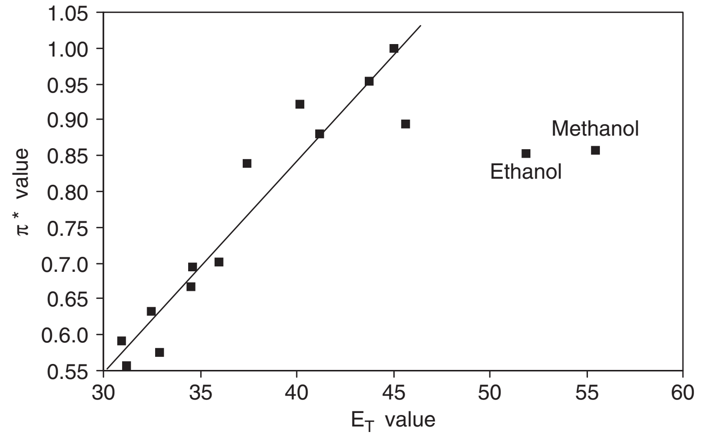


FIGURE 9.12 The relationship between the π^* and E_T values for several solvents.

reactions. For the other solvents it is evident that any correlation between reaction rates and one of the parameters should be about equally valid for the other parameter.

Figure 9.13 shows how the SPP and δ values correlate for many of the solvents listed in Table 9.1. When the points for diethyl ether, dichloromethane, benzonitrile, ethanol, and methanol (some of which have been described by others as not fitting the usual relationships well) are deleted,

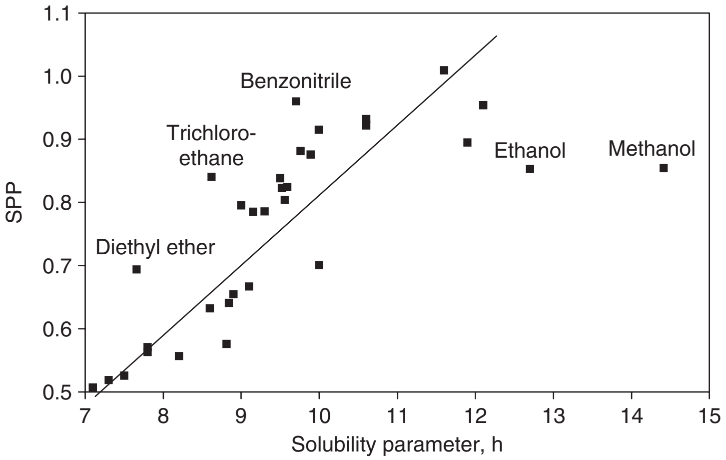


FIGURE 9.13 Correlation between SPP values and solubility parameters for solvents listed in Table 9.1.

the relationship established by means of linear regression has a correlation coefficient of 0.901. The fact that the parameters are related in this way suggests that correlations between rate constants and either of the scales would be about equally valid.

In terms of its character as a Lewis acid, the Co^{3+} ion is considered as a hard species according to the classification of Pearson (see Chapter 5). As a result, Co^{3+} bonds preferentially to hard Lewis bases such as NH_3. When comparing the electron donor properties of SCN^-, the sulfur end is soft but the nitrogen end is hard. Therefore, toward Co^{3+} the preferred bonding is $Co^{3+}{-}NCS$. However, when Co^{3+} is already bonded to five other CN^- (soft) ligands, the complex obtained is $(CN)_5Co{-}SCN$. The five CN^- ligands have "softened" the hard Co^{3+} to the point where it behaves as if it were a soft electron acceptor. This is known as the *symbiotic effect*, and it refers to the fact that the metal ion and five CN^- ligands work together in symbiosis to establish the electron character that the next ligand will encounter as it attaches.

Undoubtedly, similar effects occur in relationship to the formation of solvated transition states. Solvent molecules that are bound to the reactant molecules or ions as they undergo reaction have somewhat different properties from those of the bulk solvent. Permanent dipole moments can become larger due to the induction effects produced by charge centers in the transition state. Ordering of solvent molecules as a result of electrostriction undoubtedly causes the dielectric constant of the solvent to change in the vicinity of a solvent molecule (such as a transition state). It is for these reasons and others that a simple approach to correlating rate constants for a reaction carried out in a series of solvents to properties of the solvents is likely to be useful but far from exact. Simply because of the energies involved, spectroscopic transitions involving electrons in orbitals located on selected molecules used as probes to determine solvent effects are likely to be less subject to symbiotic effects than are properties such as assisting the formation of a transition state. The transition state in a reaction is a structure that changes with time (of course, a very short time), so the effect produced by the solvent is some sort of a "weighted average" interaction. In spite of this difficulty, some of the correlations between rate constants using the E_T, SPP, and π^* indices have been good and some have been very good.

The interaction of several types of species in solution can be considered as special cases of Lewis acid-base behavior. Depending on the nature of the species, the interaction may be primarily the result of electrostatic attraction or the result of covalent bonding. In many cases, both factors come into

play, so the total interaction can be described as resulting from both types of bonding. One approach to take to describe such interactions is that of Drago (1973) who express the heat of interaction as

$$-\Delta H_{AB} = E_A E_B + C_A C_B \tag{9.39}$$

In this equation, ΔH_{AB} is the enthalpy change for the formation of an acid-base adduct AB, E_A and E_B are parameters that express the electrostatic bonding capabilities of the acid and base, and C_A and C_B are parameters that relate to the covalent bonding tendencies of the acid and base. The product of the electrostatic parameters gives the enthalpy change due to ionic contributions to the bonding, while the product of the covalent parameters gives the covalent contribution. The total bond enthalpy is the sum of the two terms that represent two types of contributions to the bond. However, the enthalpy data and parameters correlated by this equation were derived for systems in which the donor-acceptor interaction involves essentially no nonspecific interaction. Drago (1992) also developed a correlation that is expressed by the equation

$$\Delta_\chi = S'P + W \tag{9.40}$$

in which S' is a solvent parameter that presumably measures polarity, P is a parameter for the probe molecules, and W is a gas phase value for the parameter (such as spectral position). However, this equation was based on data for "systems devoid of specific donor-acceptor interactions (including π-stacking) . . . ". This model can be used to predict spectral shifts for many systems. Drago has reasoned that the fact that the same S' parameter can be used for solvents having a wide variety of structures and dimensions suggests that solvation involves a dynamic cavity model. According to this model, a cavity is formed in the solvent that leads to the most favorable nonspecific interaction between the solute and solvent. Precisely because the formation of a cavity in the solvent is hindered by high cohesion density it is reasonably to look to the solubility parameter as a means of correlating rate data. As has been shown, reasonably good correlations exist for widely differing reaction types when using solubility parameters, and many of the reactions would not be appropriate to consider as solely the result of the transition state forming due to either specific or nonspecific interactions.

One difficulty arises as a result of the fact that values for the parameters characteristic of the acid and base must be determined. However, the efforts of Drago (1973) was initially directed at correlations involving heats of formation for adducts of Lewis acids and Lewis bases when both species

were dissolved in an inert solvent. Thus, it is possible to assign values for a reference acid and base and then determine values for the constants for other acids and bases by making use of the experimental heats of reaction. Unfortunately, it is not possible to isolate a transition state and measure its heat of reaction with solvent molecules. Consequently, no consistent set of constants determined from calorimetric measurements exists for *transition states*. The result is that while it is easy to understand that the interaction of the reactants, products, and transition states with solvents involve elements of electrostatic and covalent bonding, there is no satisfactory way to determine all of the parameters, especially for the transition state. It is solvation of the transition state that affects the equilibrium concentration of that species, which in turn affects the rate of reaction. Some of the approaches taken to explain and correlate solvent effects work well, but they are essentially empirical approximations to a very complex problem.

As has been shown, rates of reactions in many solvents correlate satisfactorily with solvent parameters, of which there are many. One interesting aspect of the solubility parameter is that it includes the contributions for dipole-dipole, London, and hydrogen bonding forces (see Section 5.1.2), which is not true of all parameters used to establish polarity scales. As a result, it may have more *general* applicability when correlating rates in solvents having greatly different character because it is *not* such a restricted property. It has been communicated to the author by another kineticist that solubility parameters are not universally accepted as a means of explaining the effects of solvents on reaction rates. None of the other polarity scales is *universally* accepted either. The fact that so many types of correlations have been proposed and utilized underscores the importance of this issue and the fact that there is no universal answer to the problem.

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PROBLEMS

1. In the radioactive decay series that leads from ${}^{238}{}_{92}U$ to ${}^{206}{}_{82}Pb$, half-life for the α-decay of ${}^{226}{}_{88}Ra$ to ${}^{222}{}_{86}Rn$ is 1620 years. ${}^{222}{}_{86}Rn$ undergoes α-decay to ${}^{218}{}_{84}Po$ with a half-life of 3.82 days. Suppose a sample of pure ${}^{226}{}_{88}Ra$ contains 10^{20} atoms. How long will it be before there are 10^{18} atoms of ${}^{226}{}_{88}Ra$ remaining?

2. A certain nuclide undergoes radioactive decay by β^- emission (99.58%) and by α emission (0.42%). If the nuclide has a half-life of 18.9 minutes, what are the decay constants for each type of decay (λ_α and λ_β)?

3. For the decay scheme

$$A \xrightarrow{10.6\ \text{hr}} B \xrightarrow{1.01\ \text{hr}} C$$

determine the number of atoms of each type over the time interval of 6.00 hours if 10^4 atoms of A are present initially.

4. Consider the following decay scheme.

$${}^{214}{}_{82}Pb \xrightarrow[\beta^-]{26.8\ \text{min}} {}^{214}{}_{83}Bi \xrightarrow[\beta^-]{19.7\ \text{min}} {}^{214}{}_{84}Po$$

Describe the concentration of each species over the time interval of four half-lives of ${}^{214}{}_{82}Pb$. How many atoms of each type will be present after 125 minutes if the original sample consisted of 10^6 atoms of ${}^{214}{}_{82}Pb$ but no ${}^{214}{}_{83}Bi$ or ${}^{214}{}_{84}Po$?

5. Consider the number of π electrons to determine the mechanism for the ring thermal closure reactions of (a) butadiene and (b) octatetraene.

6. Consider the thermal ring closure of the propene cation and anion. Would the mechanism for the reactions be the same? Show the pathway for the reaction of each species.

7. Many articles are published that have the effect of solvent on reaction rate as a significant component of the work. This is particularly true of the study of reactions in organic chemistry. After examining several journals, select an article in which the role of the solvent is discussed from the standpoint of kinetics. Make sure that enough data are presented to enable you to perform the following analysis.
   (a) Study the data presented to see how reaction rates vary with the solvents chosen.
   (b) What solvent parameters were used to correlate and explain the role of the solvent? Are the conclusions presented sound and complete? Explain why or why not.
   (c) Using solvent parameters for compounds listed in Table 9.1 and other sources and the rate data given in the article you select, make your own correlations between reaction rate and the nature of the solvent.
   (d) Write a short introduction summarizing the salient kinetic aspects presented in the article. Write a longer section presenting the details of your analysis of the data. Try to expand the interpretation and conclusions of the author(s) of the paper. Make your finished document have the form of a short note or letter to the editor of a journal.

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